

(19) World Intellectual Property Organization
International BureauApplication Number: 10/631,029
Filing Date: 07/29/2003
First Named Inventor: Rajinder Singh
Attorney Docket Number: 064311-1602
Identifier: F7(43) International Publication Date
3 May 2001 (03.05.2001)

PCT

(10) International Publication Number
WO 01/30782 A2(51) International Patent Classification⁷: **C07D 498/04**,
519/00, A01N 43/90 // (C07D 498/04, 265:00, 221:00)
(C07D 519/00, 498:00, 471:00) (C07D 519/00, 498:00,
487:00) (C07D 519/00, 498:00, 498:00)

(21) International Application Number: PCT/EP00/10595

(22) International Filing Date: 27 October 2000 (27.10.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
1988/99 29 October 1999 (29.10.1999) CH(71) Applicant (for all designated States except US): **SYNGENTA PARTICIPATIONS AG** [CH/CH]; Schwarzwaldallee 215, CH-4058 Basel (CH).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **LÜTHY, Christoph** [CH/CH]; Mittelweg 1, CH-4142 Münchenstein (CH). **NEBEL, Kurt** [CH/CH]; Baselweg 32, CH-4146 Hochwald (CH). **WENGER, Jean** [CH/CH]; Zwischen den Rainen 374, CH-4323 Wallbach (CH).(74) Agent: **BECKER, Konrad**; Syngenta Participations AG, Intellectual Property, P.O. Box, CH-4002 Basel (CH).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

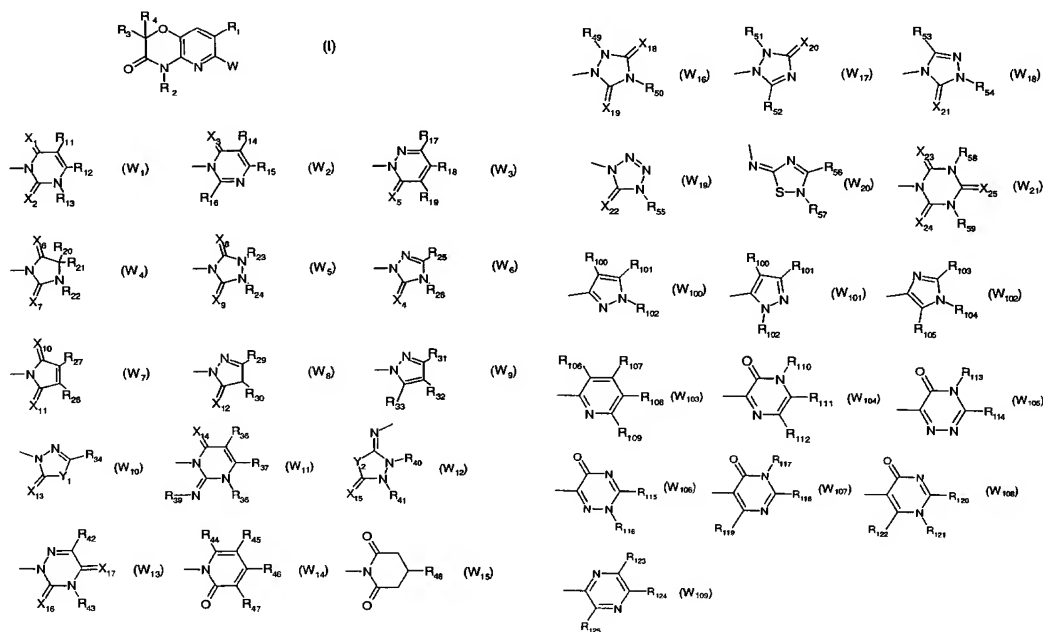
(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— Without international search report and to be republished upon receipt of that report.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: NOVEL HERBICIDES



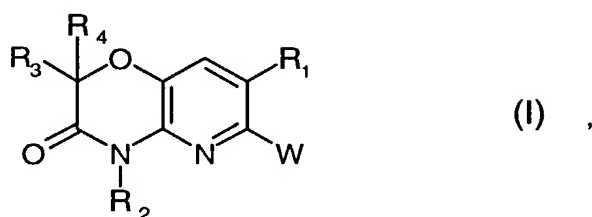
Novel herbicides

The present invention relates to novel, herbicidally active 4H-pyrido[3,2-b][1,4]oxazin-3-ones substituted by nitrogen heterocycles, to processes for the preparation thereof, to compositions comprising those compounds, and to the use thereof in the control of weeds, especially in crops of useful plants, for example cereals, maize, rice, cotton, soybeans, rape, sorghum, sugar cane, sugar beet, sunflowers, vegetables, plantation crops and fodder plants, or in the inhibition of plant growth, and also in the non-selective control of weeds.

N-Pyridyl-imides, N-pyridyl-pyrazoles and N-pyridyl-triazolidinones and also N-pyridyl-uracils and N-pyridonyl-uracils having herbicidal activity are described, for example, in DE 3 917 469, WO 98/27082, WO 98/27083, WO 98/52938, WO 98/42698, WO 98/21199, WO 99/52892 and WO 99/52893.

Novel heterocyclic derivatives of 6-amino-4H-pyrido[3,2-b][1,4]oxazin-3-one and 3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazine-6-carboxylic acid which are substituted in the 6-position and have herbicidal and growth-inhibiting properties have now been found.

The present invention accordingly relates to compounds of formula I



wherein

R₁ is hydrogen, methyl or halogen;

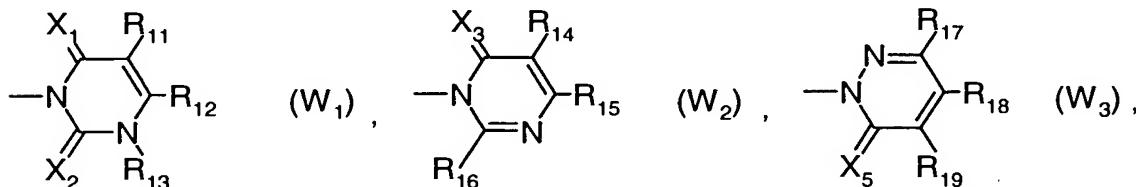
R₂ is hydrogen, C₁-C₁₂alkyl, C₁-C₁₂haloalkyl, C₂-C₁₂alkenyl, C₂-C₁₂alkynyl, C₂-C₈alkynyl-C₂-C₄alkenyl, C₃-C₁₂allenyl, C₂-C₁₂haloalkenyl, C₂-C₁₂haloalkynyl, C₃-C₆cycloalkyl, C₃-C₆cycloalkyl-C₁-C₄alkyl, C₃-C₆halocycloalkyl-C₁-C₄alkyl, tri(C₁-C₄alkyl)silyl-C₁-C₄alkyl, tri(C₁-C₄alkyl)silyl-C₂-C₄alkenyl, cyano-C₁-C₁₂alkyl, C₁-C₆alkoxy-C₁-C₄alkyl, C₁-C₄alkoxy-C₁- or -C₂-alkoxy-C₁- or -C₂-alkyl, di(C₁-C₄alkoxy)-C₁- or -C₂-alkyl, ethylenedioxy-C₁- or -C₂-alkyl, C₂-C₆alkenyloxy-C₁-C₄alkyl, C₂-C₆haloalkenyloxy-C₁-C₄alkyl, C₂-C₆alkynyloxy-C₁-C₄alkyl, C₃-C₆haloalkynyloxy-C₁-C₄alkyl, C₁-C₆alkylthio-C₁-C₄alkyl, C₁-C₆alkylsulfinyl-C₁-C₄alkyl, C₁-

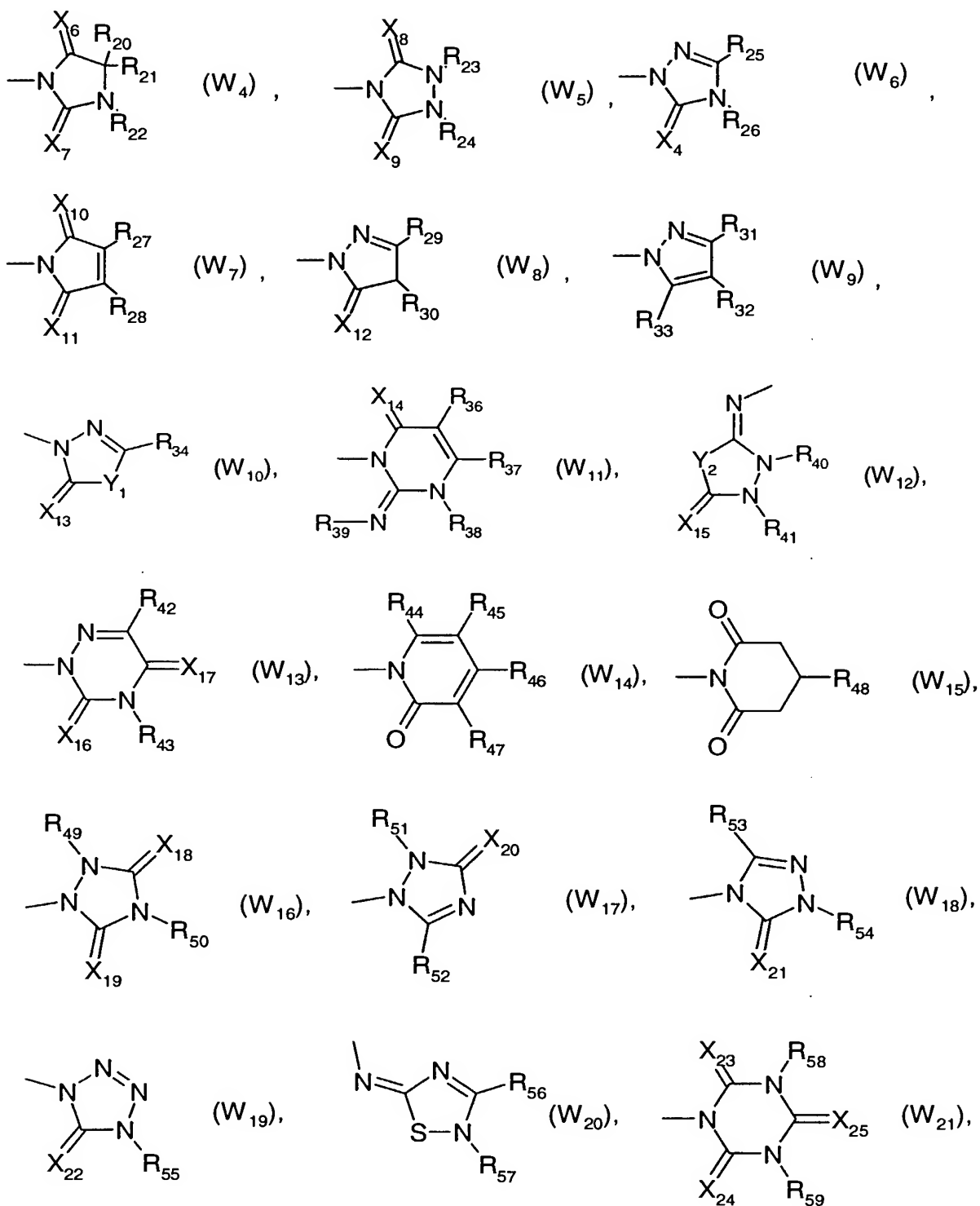
C₆alkylsulfonyl-C₁-C₄alkyl, hydroxy-C₁-C₁₂alkyl, C₁-C₆alkylcarbonyl-C₁-C₄alkyl, C₁-C₆haloalkylcarbonyl-C₁-C₄alkyl, C₁-C₆alkoxycarbonyl-C₁-C₄alkyl, C₁-C₆alkoxy-C₁- or -C₂-alkoxycarbonyl-C₁-C₄alkyl, C₁-C₆alkoxycarbonyl-C₁-C₄haloalkyl, C₃-C₆cycloalkylcarbonyl-C₁-C₄alkyl or benzoyl-C₁-C₄alkyl wherein the benzoyl group may be substituted by halogen, C₁-C₃alkyl, C₁-C₃haloalkyl, C₁-C₃alkoxy or by C₁-C₃haloalkoxy, or is C₃-C₆alkenyloxycarbonyl-C₁-C₄alkyl, C₃-C₆alkynyloxycarbonyl-C₁-C₄alkyl, C₁-C₆alkylcarbonyloxy-C₁-C₄alkyl, C₂-C₆alkenylcarbonyloxy-C₁-C₄alkyl, C₃-C₆cycloalkylcarbonyloxy-C₁-C₄alkyl, benzoyloxy-C₁-C₄alkyl, C₁-C₆alkoxycarbonyloxy-C₁-C₄alkyl, carbamoyl-C₁-C₄alkyl, C₁-C₆alkylaminocarbonyl-C₁-C₄alkyl, or phenyl- or heterocyclyl-substituted C₁-C₄alkyl wherein the phenyl and heterocyclyl groups may be substituted by halogen, C₁-C₆alkyl, C₁-C₆alkoxy, C₁-C₆haloalkyl, C₁-C₆haloalkoxy, C₂-C₆alkenyl, C₂-C₆alkynyl, C₂-C₆haloalkenyl, C₂-C₆haloalkynyl, C₃-C₆cycloalkyl-C₁-C₄alkyl, C₃-C₆halocycloalkyl-C₁-C₄alkyl, cyano-C₁-C₄alkyl, C₁-C₆alkoxy-C₁-C₄alkyl, C₁-C₆alkylthio-C₁-C₄alkyl, C₁-C₆alkylsulfinyl-C₁-C₄alkyl, C₁-C₆alkylsulfonyl-C₁-C₄alkyl, hydroxy-C₁-C₄alkyl, C₁-C₆alkylcarbonyl-C₁-C₄alkyl, C₁-C₆alkoxycarbonyl, C₁-C₆alkoxy-carbonyl-C₁-C₄alkyl, C₁-C₆alkoxycarbonyl-C₁-C₄haloalkyl, C₁-C₆alkoxycarbonyl-C₁-C₄alkoxy, C₁-C₆alkylcarbonyloxy-C₁-C₄alkyl, C₁-C₆alkoxycarbonyloxy-C₁-C₄alkyl, C₁-C₄alkoxy-C₁-C₂alkoxy-C₁-C₂alkyl, C₁-C₄alkylaminocarbonyl, C₁-C₆alkylaminocarbonyl-C₁-C₄alkoxy, phenyl, phenoxy or by benzyloxy, wherein the phenyl ring of the last three definitions may be substituted by halogen, methyl, trifluoromethyl, methylsulfonyl, methoxy, ethoxy or by cyano; or is phenyl-substituted C₂-C₄alkenyl or C₂-C₄alkynyl, wherein the phenyl group may be substituted by halogen, methyl, trifluoromethyl, methylthio, methylsulfinyl, methylsulfonyl, methoxy, ethoxy, cyano or by nitro;

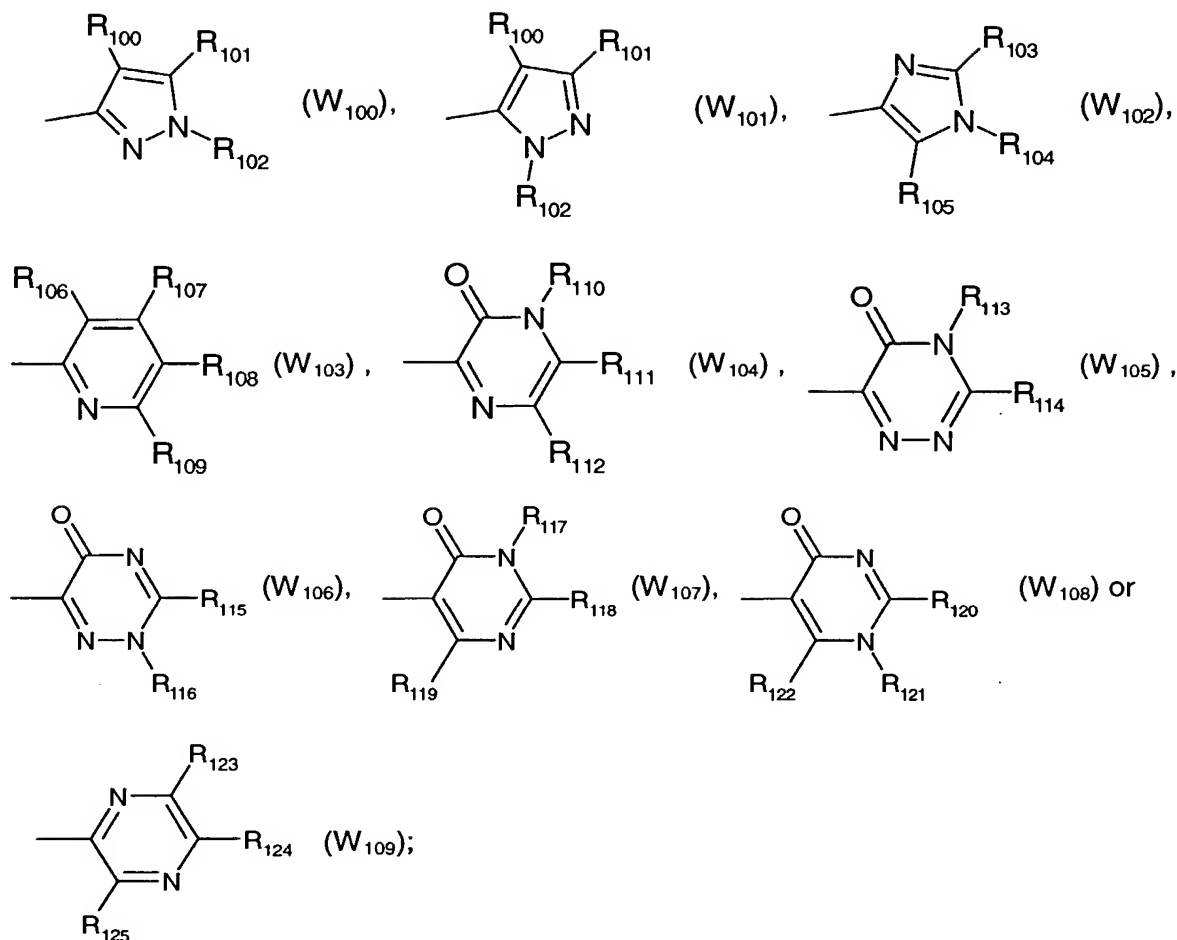
R₃ is hydrogen, C₁-C₁₂alkyl, C₁-C₁₂haloalkyl, C₁-C₆alkoxycarbonyl, or phenyl which is unsubstituted or substituted by halogen, methyl, trifluoromethyl, methylthio, methylsulfinyl, methylsulfonyl, methoxy, ethoxy, cyano or by nitro;

R₄ is hydrogen or C₁-C₆alkyl;

W is a group







R₁₁ is hydrogen, C₁-C₃alkyl, halogen, C₁-C₃haloalkyl or cyano;

R₁₂ is C₁-C₃alkyl, C₁-C₃haloalkyl, C₁-C₃alkyl-S(O)_{n1}-, C₁-C₃haloalkyl-S(O)_{n1}- or cyano;
and

R₁₃ is hydrogen, C₁-C₃alkyl, C₁-C₃haloalkyl, allyl, propargyl or amino; or

R₁₂ and R₁₁ or R₁₂ and R₁₃ together form a C₃- or C₄-alkylene bridge which may be substituted by halogen, C₁-C₃haloalkyl or by cyano;

R₁₄ is hydrogen, C₁-C₃alkyl, halogen, C₁-C₃haloalkyl or cyano; and

R₁₅ is C₁-C₃alkyl, C₁-C₃haloalkyl, C₁-C₃alkyl-S(O)_{n2}-, C₁-C₃haloalkyl-S(O)_{n2}- or cyano; or
R₁₅ and R₁₄ together form a C₃- or C₄-alkylene bridge which may be substituted by halogen, C₁-C₃haloalkyl or by cyano;

R₁₆ is hydrogen, C₁-C₃alkyl, halogen, C₁-C₃haloalkyl, C₁-C₃alkoxy, C₁-C₃haloalkoxy, hydroxy, mercapto, C₁-C₃alkylthio, C₁-C₃alkylsulfinyl, C₁-C₃alkylsulfonyl, allylthio, propargylthio, amino, C₁-C₃alkylamino, di(C₁-C₃alkyl)amino, allylamino, propargylamino or cyano;

n₁ and n₂ are 0, 1 or 2;

R₁₇ is hydrogen, C₁-C₃alkyl, halogen or cyano; and

R₁₈ is C₁-C₃alkyl, halogen, C₁-C₃haloalkyl, C₁-C₃alkylthio, C₁-C₃alkylsulfinyl, C₁-C₃alkylsulfonyl or cyano; or

R₁₈ and R₁₇ together form a C₃- or C₄-alkylene or C₃- or C₄-alkenylene bridge, both of which may be substituted by halogen, C₁-C₃alkyl or by C₁-C₃haloalkyl;

R₁₉ is hydrogen, halogen, C₁-C₃alkyl, carboxyl, C₁-C₃alkoxycarbonyl or amino; or

R₁₉ and R₁₈ together form a C₃- or C₄-alkylene or C₃- or C₄-alkenylene bridge, both of which may be substituted by halogen, C₁-C₃alkyl or by C₁-C₃haloalkyl;

R₂₀ and R₂₁ are each independently of the other hydrogen or C₁-C₄alkyl; or

R₂₀ and R₂₁ together are a group $\begin{array}{c} \text{R}_{051} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{R}_{052} \end{array}$;

R₀₅₁ and R₀₅₂ are each independently of the other hydrogen or C₁-C₄alkyl; or

R₀₅₁ and R₀₅₂ together form a C₄- or C₅-alkylene bridge;

R₀₅₂ and R₂₂ together form a C₃alkylene bridge;

R₂₂ is hydrogen or C₁-C₃alkyl; or

R₂₂ and R₂₀ or R₂₂ and R₂₁ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by halogen, C₁-C₄alkyl, C₁-C₃haloalkyl, C₂-C₄alkenyl, C₁-C₃alkoxycarbonyl, C₁-C₃alkylcarbonyloxy, C₁-C₃alkylsulfonyloxy or by hydroxy;

R₂₃ and R₂₄ are each independently of the other hydrogen, C₁-C₃alkyl, C₁-C₃haloalkyl or propargyl; or

R₂₃ and R₂₄ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by halogen, C₁-C₄alkyl, hydroxy, C₁-C₄alkoxy or by C₁-C₄alkoxy-C₁-C₄alkoxy;

R₂₅ is hydrogen, halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, C₁-C₄alkylthio, C₁-C₄haloalkylthio, C₁-C₄alkylsulfinyl, C₁-C₄haloalkylsulfinyl, C₁-C₄alkylsulfonyl, C₁-C₄haloalkylsulfonyl, hydroxy or cyano; and

R₂₆ is hydrogen, C₁-C₄alkyl or C₁-C₄haloalkyl; or

R₂₆ and R₂₅ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen,

sulfur, -S(O)-, -S(O)₂-, $\begin{array}{c} \diagup \\ \text{N} \\ \diagdown \end{array}$ -C₁-C₄alkyl or by -C(O)- and/or substituted by halogen, C₁-

C₄alkyl, C₁-C₃haloalkyl, C₂-C₄alkenyl, C₁-C₃alkoxycarbonyl, C₁-C₃alkylcarbonyloxy, C₁-C₃alkylsulfonyloxy or by hydroxy;

R₂₇ and R₂₈ are each independently of the other hydrogen or C₁-C₄alkyl; or

R₂₇ and R₂₈ together form a C₃-C₅alkylene bridge which may be substituted by halogen or by C₁-C₄alkyl and/or interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- or form a C₄alkenylene bridge which is unsubstituted or substituted by C₁-C₄alkyl;

R₂₉ and R₃₀ are each independently of the other hydrogen, C₁-C₄alkyl or C₁-C₄haloalkyl; or

R₂₉ and R₃₀ together form a C₃-C₅alkylene bridge which may be substituted by halogen or by C₁-C₄alkyl and/or interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)-;

R₃₁ is hydrogen, C₁-C₄alkyl or C₁-C₄haloalkyl; and

R₃₂ is hydrogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkylthio, C₁-C₄alkylsulfinyl, C₁-C₄alkylsulfonyl, cyano or nitro; or

R₃₁ and R₃₂ together form a C₃-C₅alkylene bridge which may be substituted by halogen or by C₁-C₄alkyl and/or interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- or form a C₄alkenylene bridge which is unsubstituted or substituted by C₁-C₄alkyl;

R₃₃ is hydrogen, C₁-C₃alkyl, halogen, C₁-C₃haloalkyl, hydroxy, C₁-C₃alkoxy, C₁-C₃haloalkoxy, mercapto, C₁-C₃alkylthio, C₁-C₃alkylsulfinyl, C₁-C₃alkylsulfonyl, amino, C₁-C₃alkylamino, C₁-C₃alkylcarbonylamino, C₁-C₃haloalkylcarbonylamino or cyano;

R₃₄ is C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄alkylthio;

R₃₆ is hydrogen, C₁-C₃alkyl, halogen, C₁-C₃haloalkyl or cyano; and

R₃₇ is C₁-C₃alkyl, C₁-C₃haloalkyl, C₁-C₃alkyl-S(O)_{n1}-, C₁-C₃haloalkyl-S(O)_{n1}- or cyano; or

R₃₇ and R₃₆ together form a C₃- or C₄-alkenylene bridge which may be substituted by halogen, C₁-C₃alkyl, C₁-C₃haloalkyl or by cyano;

R₃₈ is C₁-C₃alkyl; and

R₃₉ is hydrogen or C₁-C₃alkyl; or

R₃₉ and R₃₈ together form a C₂- or C₃-alkylene or C₂- or C₃-alkenylene bridge which is unsubstituted or substituted by C₁-C₄alkyl or form an -NH-CH₂-, -N=CH- or -N=N- bridge;

R₄₀ and R₄₁ are each independently of the other C₁-C₃alkyl or C₁-C₃haloalkyl; or

R₄₁ and R₄₀ together form a C₃-C₅alkylene bridge which is unsubstituted or substituted by halogen or by C₁-C₄alkyl;

R₄₂ is hydrogen, C₁-C₃alkyl, C₁-C₃haloalkyl, cyano or carboxyl;

R₄₃ is hydrogen, C₁-C₃alkyl, C₁-C₃haloalkyl, allyl or propargyl;

R₄₄ is hydrogen, C₁-C₃alkyl, halogen, C₁-C₃haloalkyl, hydroxy, mercapto, amino, C₁-C₃alkoxy, C₁-C₃alkylthio or di(C₁-C₄alkyl)amino;

R₄₅ is hydrogen, C₁-C₃alkyl, halogen or cyano;

R₄₆ is C₁-C₃alkyl, C₁-C₃haloalkyl or cyano;

R₄₇ is hydrogen, C₁-C₃alkyl or halogen;

R₄₈ is C₁-C₃alkyl or C₁-C₃haloalkyl;

R₄₉, R₅₀ and R₅₁ are each independently of the others hydrogen, C₁-C₄alkyl, propargyl or C₁-C₄haloalkyl;

R₅₂ is C₁-C₃alkyl, halogen, C₁-C₃haloalkyl, C₁-C₃alkoxy, C₁-C₃haloalkoxy, C₁-C₃alkylthio, C₁-C₃alkylsulfinyl, C₁-C₃alkylsulfonyl, amino or C₁-C₃alkylamino;

R₅₃ is C₁-C₃alkyl or C₁-C₃haloalkyl;

R₅₄ is C₁-C₃alkyl;

R₅₅ is hydrogen, C₁-C₃alkyl, propargyl or C₁-C₃haloalkyl;

R₅₆ is C₁-C₃alkyl, C₁-C₃haloalkyl, C₁-C₃alkylthio, C₁-C₃alkylsulfinyl or C₁-C₃alkylsulfonyl; and

R₅₇ is C₁-C₃alkyl or C₁-C₃haloalkyl; or

R₅₇ and R₅₆ together form a C₂-C₄alkylene or C₂-C₄alkenylene bridge which both are unsubstituted or substituted by halogen or by C₁-C₄alkyl;

R₅₈ is hydrogen, C₁-C₃alkyl, C₁-C₃haloalkyl or amino;

R₅₉ is hydrogen, C₁-C₃alkyl or C₁-C₃haloalkyl;

R₁₀₀ is hydrogen, halogen, nitro, amino, cyano, C₁-C₃alkyl, C₂- or C₃-alkenyl or C₂- or C₃-alkynyl;

R₁₀₁ is hydrogen, halogen, nitro, amino, cyano, hydroxy, mercapto, C₁-C₃alkyl, C₁-C₃haloalkyl, C₂- or C₃-alkenyl, C₂- or C₃-alkynyl, C₁-C₃alkoxy, C₁-C₃haloalkoxy, C₁-C₃alkylthio, C₁-C₃alkylsulfinyl, C₁-C₃alkylsulfonyl, C₁-C₃haloalkylthio, C₁-C₃haloalkylsulfinyl, C₁-C₃haloalkylsulfonyl, FS(O)₂-, ClS(O)₂-, C₁-C₆alkylsulfonyloxy, C₁-C₆haloalkylsulfonyloxy, C₁-C₃alkylcarbonyl, HC(O)-, HOC(O)-, ClC(O)-, FC(O)-, C₁-C₃alkoxycarbonyl, H₂NC(O)- or H₂NC(S)-; and

R₁₀₂ is hydrogen, C₁-C₆alkyl, C₁-C₆alkyl substituted by cyano, HO-, HOC(O)-, C₁-C₃alkoxycarbonyl or by HC(O)-, or is C₃-C₆alkenyl, C₃-C₆alkynyl, C₃-C₆cycloalkyl, C₁-C₆haloalkyl or C₁-C₃alkylsulfonyl; or

when W is a group W₁₀₀,

R₁₀₂ and R₁₀₁ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen;

R₁₀₃ is hydrogen, halogen, nitro, amino, cyano, hydroxy, mercapto, C₁-C₃alkyl, C₁-C₃haloalkyl, C₂- or C₃-alkenyl, C₂- or C₃-alkynyl, C₁-C₃alkoxy, C₁-C₃haloalkoxy, C₁-C₃alkylthio, C₁-C₃alkylsulfinyl, C₁-C₃alkylsulfonyl, C₁-C₃haloalkylthio, C₁-C₃haloalkylsulfinyl, C₁-C₃haloalkylsulfonyl, FS(O)₂-, ClS(O)₂-, C₁-C₆alkylsulfonyloxy, C₁-C₆haloalkylsulfonyloxy, C₁-C₃alkylcarbonyl, HC(O)-, HOC(O)-, ClC(O)-, FC(O)-, C₁-C₃alkoxycarbonyl, H₂NC(O)- or H₂NC(S)-;

R₁₀₄ is hydrogen, C₁-C₆alkyl, C₁-C₆alkyl substituted by cyano, HO-, HOC(O)-, C₁-C₃alkoxy-carbonyl or by HC(O)-, or is C₃-C₆alkenyl, C₃-C₆alkynyl, C₃-C₆cycloalkyl, C₁-C₆haloalkyl or C₁-C₃alkylsulfonyl; and

R₁₀₅ is hydrogen, halogen, nitro, amino, cyano, C₁-C₃alkyl, C₂- or C₃-alkenyl or C₂- or C₃-alkynyl; or

R₁₀₄ and R₁₀₃ together form a C₃-C₅alkylene bridge or a C₄alkenylene bridge which both may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen;

R₁₀₆ is hydrogen, halogen, amino, nitro, hydroxy, C₁-C₃alkyl or C₁-C₃alkoxy;

R₁₀₇ is hydrogen, halogen, amino, hydroxy, C₁-C₃alkyl, C₁-C₃haloalkyl, HC(O)-, HOC(O)-, hydroxy-C₁-C₃alkyl, C₁-C₃alkoxy or C₁-C₃haloalkoxy; and

R₁₀₈ is hydrogen, halogen, nitro, amino, cyano, HC(O)-, HOC(O)-, H₂NC(O)-, H₂NC(S)-, hydroxy, mercapto, C₁-C₃alkyl, C₁-C₃haloalkyl, C₂- or C₃-alkenyl, C₁-C₃alkoxy, C₁-C₃haloalkoxy, C₁-C₃alkylcarbonyl, C₁-C₃alkoxycarbonyl, C₁-C₃alkylthio, C₁-C₃haloalkylthio, C₁-C₃alkylsulfinyl, C₁-C₃haloalkylsulfinyl, C₁-C₃alkylsulfonyl, C₁-C₃haloalkylsulfonyl, C₁-C₃alkylsulfonyloxy or C₁-C₃haloalkylsulfonyloxy; or

R₁₀₈ and R₁₀₇ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen;

R₁₀₉ is hydrogen, halogen, amino, hydroxy, C₁-C₃alkyl, C₁-C₃haloalkyl, HC(O)-, HOC(O)-, hydroxy-C₁-C₃alkyl, C₁-C₃alkoxy or C₁-C₃haloalkoxy; or

R₁₀₉ and R₁₀₈ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen;

R₁₁₀ is hydrogen, C₁-C₃alkyl, C₁-C₃haloalkyl, C₃-C₄alkenyl or C₃-C₄alkynyl;

R₁₁₁ is hydrogen, halogen, nitro, amino, cyano, HC(O)-, HOC(O)-, H₂NC(O)-, H₂NC(S)-, hydroxy, mercapto, C₁-C₃alkyl, C₁-C₃haloalkyl, C₂- or C₃-alkenyl, C₁-C₃alkoxy, C₁-C₃haloalkoxy, C₁-C₃alkylcarbonyl, C₁-C₃alkoxycarbonyl, C₁-C₃alkylthio, C₁-C₃haloalkylthio, C₁-C₃alkylsulfinyl, C₁-C₃haloalkylsulfinyl, C₁-C₃alkylsulfonyl, C₁-C₃haloalkylsulfonyl, C₁-C₃alkylsulfonyloxy or C₁-C₃haloalkylsulfonyloxy; and

R₁₁₂ is hydrogen, halogen, amino, hydroxy, C₁-C₃alkyl, C₁-C₃haloalkyl, HC(O)-, HOC(O)-, hydroxy-C₁-C₃alkyl, C₁-C₃alkoxy or C₁-C₃haloalkoxy; or

R₁₁₁ and R₁₁₀ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein the C₃-C₅alkylene bridge is bonded to the N atom of the pyrazinone *via* a CH₂ group; or

R₁₁₂ and R₁₁₁ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen;

- R₁₁₃ is hydrogen, C₁-C₃alkyl, C₁-C₃haloalkyl, C₃-C₄alkenyl or C₃-C₄alkynyl; and
- R₁₁₄ is hydrogen, halogen, nitro, amino, cyano, HC(O)-, HOC(O)-, H₂NC(O)-, H₂NC(S)-, hydroxy, mercapto, C₁-C₃alkyl, C₁-C₃haloalkyl, C₂- or C₃-alkenyl, C₁-C₃alkoxy, C₁-C₃haloalkoxy, C₁-C₃alkylcarbonyl, C₁-C₃alkoxycarbonyl, C₁-C₃alkylthio, C₁-C₃haloalkylthio, C₁-C₃alkylsulfinyl, C₁-C₃haloalkylsulfinyl, C₁-C₃alkylsulfonyl, C₁-C₃haloalkylsulfonyl, C₁-C₃alkylsulfonyloxy, C₁-C₃haloalkylsulfonyloxy, C₁-C₃alkylamino or di(C₁-C₃alkyl)amino; or R₁₁₄ and R₁₁₃ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein the C₃-C₅alkylene bridge is bonded to the N atom of the triazinone *via* a CH₂ group;
- R₁₁₅ is hydrogen, halogen, nitro, amino, cyano, HC(O)-, HOC(O)-, H₂NC(O)-, H₂NC(S)-, hydroxy, mercapto, C₁-C₃alkyl, C₁-C₃haloalkyl, C₂- or C₃-alkenyl, C₁-C₃alkoxy, C₁-C₃haloalkoxy, C₁-C₃alkylcarbonyl, C₁-C₃alkoxycarbonyl, C₁-C₃alkylthio, C₁-C₃haloalkylthio, C₁-C₃alkylsulfinyl, C₁-C₃haloalkylsulfinyl, C₁-C₃alkylsulfonyl, C₁-C₃haloalkylsulfonyl, C₁-C₃alkylsulfonyloxy or C₁-C₃haloalkylsulfonyloxy; and
- R₁₁₆ is hydrogen, C₁-C₃alkyl, C₁-C₃haloalkyl, C₃-C₄alkenyl or C₃-C₄alkynyl; or R₁₁₆ and R₁₁₅ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein the C₃-C₅alkylene bridge is bonded to the N atom of the triazinone *via* a CH₂ group;
- R₁₁₇ is hydrogen, C₁-C₃alkyl, C₁-C₃haloalkyl, C₃-C₄alkenyl or C₃-C₄alkynyl;
- R₁₁₈ is hydrogen, halogen, nitro, amino, cyano, HC(O)-, HOC(O)-, H₂NC(O)-, H₂NC(S)-, hydroxy, mercapto, C₁-C₃alkyl, C₁-C₃haloalkyl, C₂- or C₃-alkenyl, C₁-C₃alkoxy, C₁-C₃haloalkoxy, C₁-C₃alkylcarbonyl, C₁-C₃alkoxycarbonyl, C₁-C₃alkylthio, C₁-C₃haloalkylthio, C₁-C₃alkylsulfinyl, C₁-C₃haloalkylsulfinyl, C₁-C₃alkylsulfonyl, C₁-C₃haloalkylsulfonyl, C₁-C₃alkylsulfonyloxy or C₁-C₃haloalkylsulfonyloxy; and
- R₁₁₉ is hydrogen, halogen, amino, nitro, hydroxy, C₁-C₃alkyl or C₁-C₃alkoxy; or R₁₁₈ and R₁₁₇ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein the C₃-C₅alkylene bridge is bonded to the N atom of the pyrimidinone *via* a CH₂ group;
- R₁₂₀ is hydrogen, halogen, nitro, amino, cyano, HC(O)-, HOC(O)-, H₂NC(O)-, H₂NC(S)-, hydroxy, mercapto, C₁-C₃alkyl, C₁-C₃haloalkyl, C₂- or C₃-alkenyl, C₁-C₃alkoxy, C₁-C₃haloalkoxy, C₁-C₃alkylcarbonyl, C₁-C₃alkoxycarbonyl, C₁-C₃alkylthio, C₁-C₃haloalkylthio, C₁-C₃alkylsulfinyl, C₁-C₃haloalkylsulfinyl, C₁-C₃alkylsulfonyl, C₁-C₃haloalkylsulfonyl, C₁-C₃alkylsulfonyloxy or C₁-C₃haloalkylsulfonyloxy;
- R₁₂₁ is hydrogen, C₁-C₃alkyl, C₁-C₃haloalkyl, C₃- or C₄-alkenyl or C₃- or C₄-alkynyl; and
- R₁₂₂ is hydrogen, halogen, amino, nitro, hydroxy, C₁-C₃alkyl or C₁-C₃alkoxy; or

R₁₂₁ and R₁₂₀ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein the C₃-C₅alkylene bridge is bonded to the N atom of the pyrimidinone *via* a CH₂ group;

R₁₂₃ is hydrogen, C₁-C₃alkyl, halogen or C₁-C₃haloalkyl;

R₁₂₄ is hydrogen, halogen, nitro, amino, cyano, HC(O)-, HOC(O)-, H₂NC(O)-, H₂NC(S)-, hydroxy, mercapto, C₁-C₃alkyl, C₁-C₃haloalkyl, C₂- or C₃-alkenyl, C₁-C₃alkoxy, C₁-C₃haloalkoxy, C₁-C₃alkylcarbonyl, C₁-C₃alkoxycarbonyl, C₁-C₃alkylthio, C₁-C₃haloalkylthio, C₁-C₃alkylsulfinyl, C₁-C₃haloalkylsulfinyl, C₁-C₃alkylsulfonyl, C₁-C₃haloalkylsulfonyl, C₁-C₃alkylsulfonyloxy or C₁-C₃haloalkylsulfonyloxy; and

R₁₂₅ is hydrogen, C₁-C₃alkyl, halogen, hydroxy, C₁-C₃alkoxy, C₁-C₃haloalkoxy, C₁-C₃alkylthio, C₁-C₃alkylsulfinyl, C₁-C₃alkylsulfonyl, amino or cyano;

X₁, X₂, X₃, X₄, X₅, X₆, X₇, X₈, X₉, X₁₀, X₁₁, X₁₂, X₁₃, X₁₄, X₁₅, X₁₆, X₁₇, X₁₈, X₁₉, X₂₀, X₂₁, X₂₂, X₂₃, X₂₄ and X₂₅ are each independently of the others oxygen or sulfur; and

Y₁ and Y₂ are oxygen or sulfur,

and also the agrochemically acceptable salts and tautomers, enantiomers and stereoisomers of the compounds of formula I.

In the above definitions, halogen is to be understood as being iodine and also, preferably, fluorine, chlorine or bromine.

The alkyl, alkenyl and alkynyl groups appearing in the substituent definitions may be straight-chained or branched, that especially also being true of the alkyl, alkenyl and alkynyl moiety of alkylcarbonyl, alkylcarbonyloxy, alkoxycarbonyl, alkenyloxycarbonyl, alkylS(O)_{n2}, alkylsulfonyloxy, alkylthioalkyl, alkoxyalkyl, alkoxyalkoxyalkyl, alkylamino and other alkyl-containing groups. Alkyl groups are, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl and the various isomeric pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl and dodecyl radicals. Preference is given to lower alkyl groups, for example methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, 2-pentyl and 3-pentyl.

There may be mentioned as examples of alkenyl groups vinyl, allyl, methallyl, 1-methylvinyl, but-3-en-2-yl, n-pent-4-enyl and 2-hexen-5-yl; preferably alkenyl radicals having a chain length of from 3 to 5 carbon atoms. Longer chain alkenyl groups may also contain two or more unsaturated C=C bond groups, for example C₂-C₈alkenyl-C₂-C₄alkenyl (for example substituent R₂).

There may be mentioned as examples of alkynyl radicals ethynyl, propargyl, 2-butyne-1-yl, 2-butyne-3-yl, but-2-yn-1-yl, but-3-yn-2-yl, 2-methyl-but-3-yn-2-yl, pent-4-yn-1-yl, hex-4-yn-2-yl and 3-heptyne-2-yl; preferably alkynyl radicals having a chain length of from 3 to 5 carbon atoms.

Suitable haloalkyl radicals include alkyl groups substituted one or more times, especially from one to five times, by halogen, halogen being in particular iodine and especially fluorine, chlorine or bromine, for example fluoromethyl, difluoromethyl, trifluoromethyl, chloromethyl, dichloromethyl, difluorochloromethyl, 1-fluoroethyl, 2-fluoroethyl, 1,1-difluoroethyl, 2,2-difluoroethyl, 2,2,2-trifluoroethyl, 2,2,2-difluorochloroethyl, 2-chloroethyl, 2-bromoethyl, pentafluoroethyl, 2-fluoroprop-1-yl, 3-fluoroprop-1-yl, 3,3-difluoroprop-1-yl and 2,3,3-trifluoroprop-1-yl.

Suitable haloalkenyl radicals include alkenyl groups substituted one or more times by halogen, halogen being in particular bromine or iodine and especially fluorine or chlorine, for example 2- and 3-fluoropropenyl, 2- and 3-chloropropenyl, 2- and 3-bromopropenyl, 2,3,3-trifluoropropenyl, 2,3,3-trichloropropenyl, 4,4,4-trifluorobut-2-en-1-yl and 4-chlorobut-2-en-1-yl. Preferred alkenyl radicals substituted once, twice or three times by halogen are especially those having a chain length of 3 or 5 carbon atoms. The alkenyl groups may be substituted by halogen at saturated or unsaturated carbon atoms and may optionally occur in the *cis* and also *trans* forms.

Suitable haloalkynyl radicals include alkynyl groups substituted one or more times by halogen, halogen being in particular bromine or iodine and especially fluorine or chlorine, for example 3-fluoropropynyl, 3-chloropropynyl, 3-bromopropynyl, 3,3,3-trifluoropropynyl and 4,4,4-trifluorobut-2-yn-1-yl. Preferred alkynyl groups substituted one or more times by halogen are those having a chain length of from 3 to 5 carbon atoms.

There may be mentioned as examples of cycloalkyl- and halocycloalkyl-containing groups the cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl group.

Cycloalkylalkyl is, for example, cyclopropylmethyl, dimethylcyclopropylmethyl, difluorocyclopropylmethyl, dichlorocyclopropylmethyl, dibromocyclopropylmethyl, 2,2,3,3-tetrafluorocyclobutylmethyl and 2,2-difluoro-3,3-dichlorocyclobutylmethyl.

The cycloalkyl-containing groups and also any alkylene- or alkenylene-containing groups, for example C₃- or C₄-alkylene or C₃- or C₄-alkenylene bridges, may also be substituted one

or more times by further C₁-C₃alkyl groups, especially methyl groups, and by halogen and C₁-C₃haloalkyl.

The alkylene and alkenylene bridges, for example in the definitions 'R₁₅ and R₁₄ together form a C₃- or C₄-alkylene bridge' or 'R₁₈ and R₁₇ together form a C₃- or C₄-alkylene or C₃- or C₄-alkenylene bridge' may, as mentioned in the corresponding definitions, be substituted or unsubstituted.

Likewise, in the definitions 'R₂₇ and R₂₈ together form a...', 'R₂₉ and R₃₀ together form a...', 'R₃₁ and R₃₂ together form a...', and 'R₄₁ and R₄₀ together form a C₃-C₅alkylene bridge', and 'R₃₉ and R₃₈ together form a C₂- or C₃-alkylene bridge' and 'R₅₇ and R₅₆ together form a C₂-C₄alkylene bridge', those alkylene bridges may be substituted by halogen, C₁-C₄alkyl or by C₁-C₃haloalkyl.

Especially in the definitions 'R₂₂ and R₂₀ together form a ...', 'R₂₂ and R₂₁ together form a...', 'R₂₃ and R₂₄ together form a...', 'R₂₆ and R₂₅ together form a...', 'R₂₇ and R₂₈ together form a...', 'R₂₉ and R₃₀ together form a...', 'R₃₁ and R₃₂ together form a...' and 'R₄₁ and R₄₀ together form a C₃-C₅alkylene bridge', and also 'R₃₉ and R₃₈ together form a C₂- or C₃-alkylene bridge' and 'R₅₇ and R₅₆ together form a C₂-C₄alkylene bridge', a carbon atom of such a bridge may be substituted once or twice, geminally or vicinally, by fluorine.

Alkylsulfonyl is, for example, methylsulfonyl, ethylsulfonyl, propylsulfonyl, isopropylsulfonyl, n-butylsulfonyl, isobutylsulfonyl, sec-butylsulfonyl and tert-butylsulfonyl; preferably methylsulfonyl or ethylsulfonyl.

Haloalkylsulfonyl is, for example, fluoromethylsulfonyl, difluoromethylsulfonyl, trifluoromethylsulfonyl, chloromethylsulfonyl, trichloromethylsulfonyl, 2-fluoroethylsulfonyl, 2,2,2-trifluoroethylsulfonyl and 2,2,2-trichloroethylsulfonyl.

Alkylcarbonyl is, for example, acetyl, propionyl, pivaloyl and n-propylcarbonyl.

Haloalkylcarbonyl is especially chloromethylcarbonyl, bromomethylcarbonyl, trifluoroacetyl, dichloroacetyl, trichloroacetyl, 1-chloroethylcarbonyl, 1-bromoethylcarbonyl and 3,3,3-trifluoropropionyl.

Alkoxy *per se* and alkoxy-containing groups are especially methoxy, ethoxy and propoxy groups.

Alkenyloxy and alkynyloxy *per se* and alkenyloxy- and alkynyloxy-containing groups are especially allyloxy and propargyloxy groups.

Haloalkoxy and haloalkoxy-containing groups are especially the fluoromethoxy, difluoromethoxy, trifluoromethoxy, 2,2,2-trifluoroethoxy, 2-chloroethoxy and 2-fluoroethoxy groups.

Alkoxyalkyl is, for example, methoxymethyl, methoxyethyl, ethoxymethyl, ethoxyethyl, n-propoxymethyl, n-propoxyethyl, isopropoxymethyl and isopropoxyethyl.

Alkenyloxyalkyl is, for example, allyloxy-methyl, methallyloxy-methyl, allyloxy-ethyl and methallyloxy-ethyl.

Haloalkenyloxyalkyl is, for example, 3-chloropropenyloxy-methyl and 3-fluoropropenyloxy-methyl.

Alkynyloxyalkyl is, for example, propargyloxy-methyl, propargyloxy-ethyl, 1-methylpropargyloxy-ethyl and methylpropargyloxy-methyl.

Haloalkynyloxyalkyl is, for example, 3-chloropropynyloxy-methyl and 3-fluoropropynyloxy-methyl.

Alkoxy carbonyl is, for example, methoxycarbonyl, ethoxycarbonyl, n-propoxycarbonyl, isopropoxycarbonyl and n-butoxycarbonyl, preferably methoxycarbonyl and ethoxycarbonyl.

Alkenyloxy carbonyl is, for example, allyloxy carbonyl, methallyloxy carbonyl, 1-propenyloxy carbonyl and (but-2-en-1-yl)oxy carbonyl.

Alkynyloxy carbonyl is, for example, propargyloxy carbonyl, (but-3-yn-2-yl)oxy carbonyl and (2-methyl-but-3-yn-2-yl)oxy carbonyl.

Alkylamino is, for example, methylamino, ethylamino, n-propylamino and isopropylamino.

Alkylthio is, for example, methylthio, ethylthio, propylthio and isopropylthio.

Alkylthioalkyl is, for example, methylthioethyl, ethylthioethyl, methylthiopropyl and ethylthiopropyl.

Haloalkylthio is, for example, fluoromethylthio, difluoromethylthio, trifluoromethylthio, chloromethylthio, 2-fluoroethylthio, 2,2,2-trifluoroethylthio and 2,2,2-trichloroethylthio.

Alkylsulfinyl, alkylsulfinylalkyl, alkylsulfonyl and alkylsulfonylalkyl are, for example, methylsulfinyl, ethylsulfinyl, methylsulfinylethyl, ethylsulfinylethyl, methylsulfonyl, n-propylsulfonyl, methylsulfonylethyl and ethylsulfonylethyl.

Haloalkylsulfinyl is, for example, fluoromethylsulfinyl, difluoromethylsulfinyl, trifluoromethylsulfinyl, chloromethylsulfinyl, trichloromethylsulfinyl, 2-fluoroethylsulfinyl and 2,2,2-trifluoroethylsulfinyl.

Hydroxyalkyl is, for example, 2-hydroxyethyl, 3-hydroxypropyl and 2,3-dihydroxypropyl.

Cyanoalkyl is especially cyanomethyl, cyanoethyl, 1-cyanoethyl and 2-cyanopropyl.

A phenyl, benzoyl or heterocyclyl group can be substituted one or more times in dependence upon the substituents indicated; for example, a phenyl or benzoyl ring may be perfluoridated, or carry from 1 to 3 chlorides, alkyl, alkoxy and/or haloalkoxy groups, 1 or 2 bromides and/or nitro groups, and/or 1 cyano and/or haloalkyl group. Heterocyclyl groups may generally be occupied once or twice by the substituents indicated.

A heterocyclyl group may be aromatic and also partially or completely saturated and contain from 1 to 4 nitrogen atoms and/or 1 or 2 oxygen atoms or 1 or 2 sulfur atoms. Examples that may be mentioned include the 2- and 3-pyridyl group, the 2- and 4-pyrimidinyl group, the 1- and 3-pyrazolyl group, the 1- and 2-furyl group, the 1- and 2-thienyl group, the 2-oxazolyl group, the 1-oxadiazolyl group, the 1,2-oxazol-3-yl group, the 1,2-oxazolin-3-yl group, the 1- and 3-triazolyl group, the oxiran-2-yl group, the oxetan-3-yl group, the tetrahydrofur-2-yl group, the tetrahydropyran-2-yl group, the 1,3-dioxazolin-2-yl group, the 1,3-dioxolan-2-yl group and the 1,3-oxathiazol-2-yl group, and also the 4H-pyrido[3,2-b][1,4]oxazin-3-on-2-yl group.

Corresponding meanings may also be given to the substituents in combined definitions, for example alkynylalkenyl, cyanoalkyl, alkoxyalkoxyalkyl, di(alkoxy)alkyl, alkylthioalkyl, alkylsulfinylalkyl, alkylsulfonylalkyl, hydroxyalkyl, alkylcarbonylalkyl, haloalkylcarbonylalkyl, alkoxyalkonylalkyl, alkoxyalkonylhaloalkyl, alkenyloxyalkonylalkyl, alkynyloxyalkonylalkyl, alkylcarbonyloxyalkyl, alkenylcarbonyloxyalkyl, cycloalkylcarbonyloxyalkyl, benzoyloxyalkyl, alkoxyalkonyloxyalkyl, cycloalkylcarbonyloxyalkyl, benzoyloxyalkyl, alkylaminocarbonylalkyl, halocycloalkylalkyl, alkylcarbonylamino, alkylsulfonyloxy and haloalkylsulfonyloxy.

In the definitions of cyanoalkyl, alkylcarbonyl, alkenylcarbonyl, alkoxyalkonyl, alkenyloxyalkonyl, cycloalkylcarbonyl, alkylaminocarbonyl and haloalkylcarbonyl, the carbon atom of the cyano or carbonyl is not included in the lower and upper limits given for the number of carbons in each particular case.

L_1 in the reagents $R_{13}-L_1$ of formula IX, R_5-L_1 of formula IXb (Reaction Scheme 1) and $R_{38}-L_1$ of formula IXa, L_2 in the reagent R_2-L_2 of formula IV (Reaction Schemes 1 and 1a), L_3 in the reagent $R_{23}-L_3$ of formula XVa (Reaction Scheme 5), L_4 in the reagent $R_{24}-L_4$ of formula XVb (Reaction Scheme 5), L_5 in the reagents $R_{22}-L_5$ of formula X (Reaction Scheme 4) and $R_{26}-L_5$ of formula Xa and L_{10} in the reagent $R_{102}-L_{10}$ of formula XVI are leaving groups, for example halogen, especially chlorine, bromine or iodine, or sulfonate, especially $CH_3S(O)_2O-$ (mesyloxy) or $p\text{-tolyl-S}(O)_2O-$ (tosyloxy).

L_6 and L_7 in the reagent of formula XXXVI (Reaction Scheme 8) are leaving groups, for example halogen, especially chlorine or bromine, or, in the case of L_7 , also hydroxy or alkoxy.

L_9 in the reagent of formula XII (Reaction Schemes 1f and 22) is a leaving group, for example halogen, especially chlorine or bromine, or sulfonate, especially mesyloxy, tosyloxy or trifluoromethanesulfonyloxy.

L_{11} in the reagent of formula XXV (Reaction Scheme 17) is a leaving group, for example hydroxy, C_1-C_3 alkoxy, chlorine, amino or C_1-C_3 alkylamino.

L_{12} and L_{13} in the reagents of formulae XXVIa, XXVIb, XXVIc and XXVI d (Reaction Scheme 17) are leaving groups, for example chlorine, bromine or iodine, or a sulfonate, especially mesyloxy or tosyloxy.

L_{14} in the reagent of formula XIVa (Reaction Scheme 18) is a leaving group, for example halogen, e.g. chlorine or bromine.

L_{15} in the reagent of formula XVII (Reaction Scheme 18) is a leaving group, for example halogen, especially chlorine, bromine or iodine, or a sulfonate, especially mesyloxy or tosyloxy.

A_0 in the compound of formula IIz (Reaction Scheme 15a) is preferably methyl, chlorine, bromine or carboxy.

A_1 in the compound of formula IIb (Reaction Scheme 1c) is a leaving group, for example halogen, especially fluorine, chlorine or bromine, alkylsulfonyl, especially methylsulfonyl, sulfonate, especially mesyloxy, trifluoromethylsulfonyloxy or phenylsulfonyloxy, or nitro.

A₂ in the compound of formula IIu (Reaction Scheme 1d) is methyl, cyano, formyl, C₁-C₄alkylcarbonyl, carboxyl or C₁-C₄alkoxycarbonyl.

A₃ in the compound of formula IIv (Reaction Scheme 1e) is either a leaving group, for example halogen, especially chlorine or bromine, or a sulfonate group, especially trifluoromethylsulfonyloxy or a C₁-C₄trialkylstannyl or boronic acid group.

B in the reagent B-W of formula V (Reaction Scheme 1e) is, complementarily to A₃ in the compound of formula IIv, either a C₁-C₄trialkylstannyl or a boronic acid group, or a leaving group, for example halogen, especially chlorine or bromine, or a sulfonate group, especially trifluoromethylsulfonyloxy.

Z₁ in the reagent of formula XXXII (Reaction Scheme 15) is a leaving group, for example alkoxy, especially methoxy or ethoxy, or halogen, especially chlorine or bromine.

Z₂ in the reagent of formula XXXII (Reaction Scheme 15) is a leaving group, for example halogen, especially chlorine or bromine, or a sulfonate, especially mesyloxy or phenylsulfonyloxy.

The invention relates also to the salts that the compounds of formula I having acid hydrogen, including especially the carboxylic acid derivatives, for example hydrolysis products of R₂, to which the present invention also relates, are able to form with bases. Those salts are, for example, alkali metal salts, e.g. sodium and potassium salts; alkaline earth metal salts, e.g. calcium and magnesium salts; ammonium salts, *i.e.* unsubstituted ammonium salts and mono- or poly-substituted ammonium salts, e.g. triethylammonium and diisopropylammonium salts; or salts with other organic bases.

Among the alkali metal and alkaline earth metal hydroxides used as salt formers, emphasis is to be given to, for example, the hydroxides of lithium, sodium, potassium, magnesium and calcium, but especially those of sodium and potassium. Suitable salt formers are described, for example, in WO 97/41112.

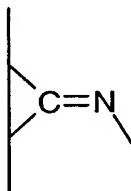
Examples of suitable amines for ammonium salt formation that come into consideration are ammonia as well as primary, secondary and tertiary C₁-C₁₈alkylamines, C₁-C₄hydroxyalkylamines and C₂-C₄alkoxyalkylamines, for example methylamine, ethylamine, n-propylamine,

isopropylamine, the four butylamine isomers, n-amylamine, isoamylamine, hexylamine, heptylamine, octylamine, nonylamine, decylamine, pentadecylamine, hexadecylamine, heptadecylamine, octadecylamine, methyl-ethylamine, methyl-isopropylamine, methyl-hexylamine, methyl-nonylamine, methyl-pentadecylamine, methyl-octadecylamine, ethyl-butylamine, ethyl-heptylamine, ethyl-octylamine, hexyl-heptylamine, hexyl-octylamine, dimethylamine, diethylamine, di-n-propylamine, diisopropylamine, di-n-butylamine, di-n-amylamine, diisoamylamine, dihexylamine, diheptylamine, dioctylamine, ethanolamine, n-propanolamine, isopropanolamine, N,N-diethanolamine, N-ethylpropanolamine, N-butyl-ethanolamine, allylamine, n-butenyl-2-amine, n-pentenyl-2-amine, 2,3-dimethylbutenyl-2-amine, dibutenyl-2-amine, n-hexenyl-2-amine, propylenediamine, trimethylamine, triethylamine, tri-n-propylamine, triisopropylamine, tri-n-butylamine, triisobutylamine, tri-sec-butylamine, tri-n-amylamine, methoxyethylamine and ethoxyethylamine; heterocyclic amines, for example pyridine, quinoline, isoquinoline, morpholine, thiomorpholine, piperidine, pyrrolidine, indoline, quinuclidine and azepine; primary arylamines, for example anilines, methoxyanilines, ethoxyanilines, o-, m- and p-toluidines, phenylenediamines, benzidines, naphthylamines and o-, m- and p-chloroanilines; but especially triethylamine, isopropylamine and diisopropylamine.

The presence of an asymmetric carbon atom in the compounds of formula I, for example in the substituent R_2 , R_3 and R_4 and also at the R_3 - and R_4 -carrying oxazine carbon atom and, in general, in alkylsulfinyl groups, wherein R_2 , R_3 or R_4 is especially a branched alkyl, alkenyl, haloalkyl, alkoxyalkyl, alkoxycarbonylalkyl or alkylsulfinylalkyl group, means that the compounds may be in the form of optically active individual isomers or in the form of racemic mixtures. In the present invention, 'compounds of formula I' is to be understood as including both the pure optical antipodes and the racemates or diastereoisomers or mixtures thereof.

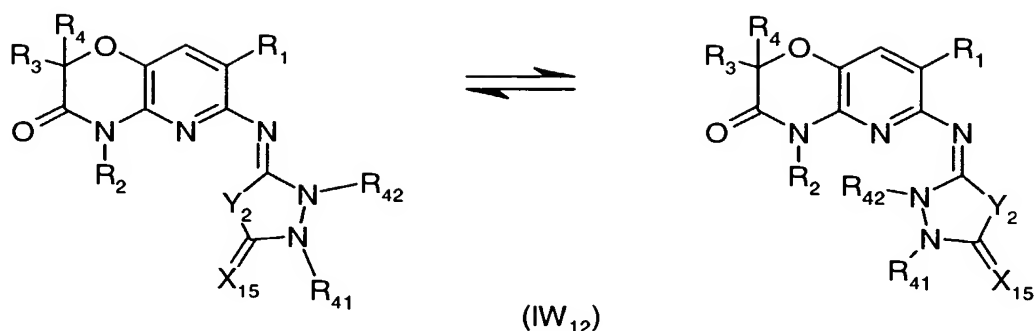
When an aliphatic C=C double bond is present, for example in alkenyl and haloalkenyl groups of the substituent R_2 , geometric <E/Z>-isomerism may occur. Likewise, in the groups

W_{11} , W_{12} and W_{20} the exocyclic double bond



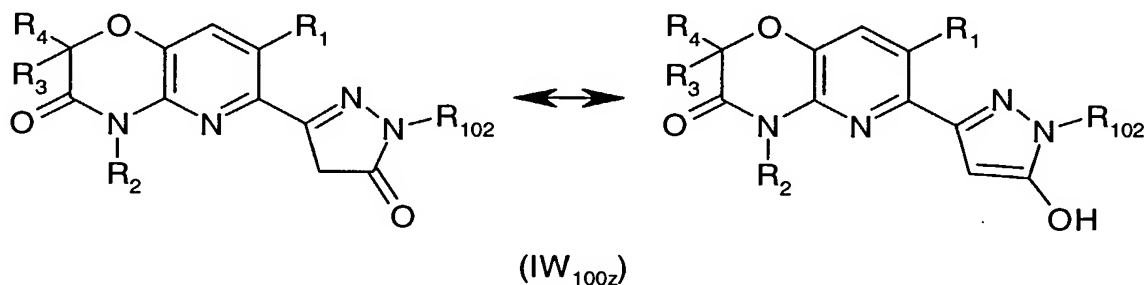
may be present in the syn/anti

form, as shown by way of example for the compound of formula IW₁₂:



Specific <E>- or <Z>-isomers of that kind can, if desired, be isolated in the pure form.

Moreover, for example, the compounds of formulae IW_{100z} and IW_{101z} can, with respect to the groups W₁₀₀ and W₁₀₁, wherein R₁₀₀ is hydrogen and R₁₀₁ is hydroxy, be present as keto-enol tautomer mixtures; for the group W_{100z} in the compound of formula IW_{100z} by way of example:



The present invention also includes those specific <E>- and <Z>-isomers, or syn- and anti-isomers, and tautomeric forms and mixtures thereof.

Preference is given to compounds of formula I wherein

R₁ is hydrogen, methyl or halogen;

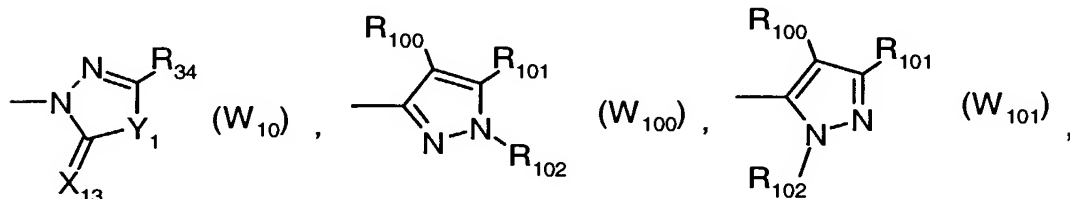
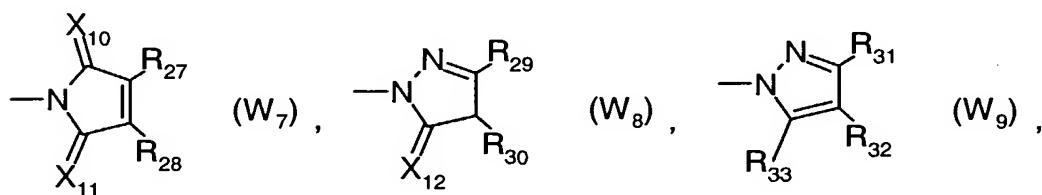
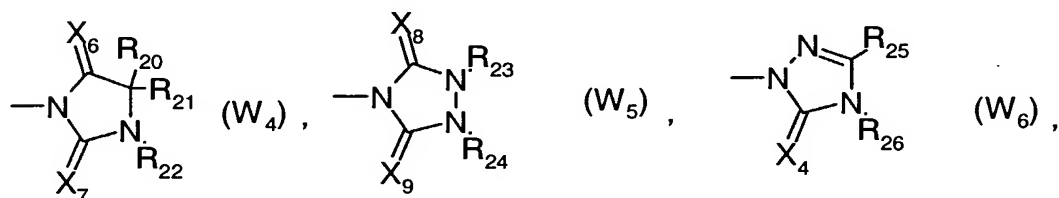
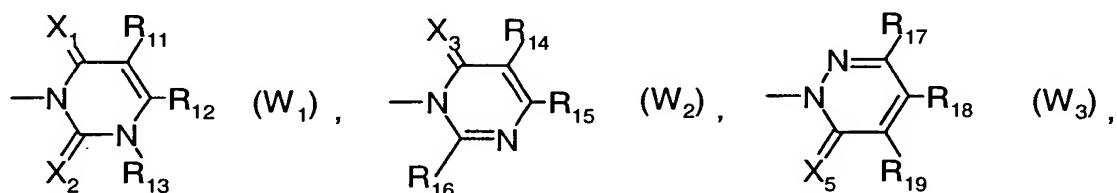
R₂ is hydrogen, C₁-C₁₂alkyl, C₁-C₁₂haloalkyl, C₁-C₁₂alkenyl, C₁-C₁₂alkynyl, C₁-C₁₂haloalkenyl, C₁-C₁₂haloalkynyl, C₁-C₆cycloalkyl-C₁-C₄alkyl, C₁-C₆halocycloalkyl-C₁-C₄alkyl, cyano-C₁-C₁₂alkyl, C₁-C₆alkoxy-C₁-C₄alkyl, C₁-C₄alkoxy-C₁-C₂alkoxy-C₁-C₂alkyl, di(C₁-C₄alkoxy)C₁-C₂alkyl, C₁-C₆alkylthio-C₁-C₄alkyl, C₁-C₆alkylsulfinyl-C₁-C₄alkyl, C₁-C₆alkylsulfonyl-C₁-C₄alkyl, hydroxy-C₁-C₁₂alkyl, C₁-C₆alkylcarbonyl-C₁-C₄alkyl, C₁-C₆haloalkylcarbonyl-C₁-C₄alkyl, C₁-C₆alkoxycarbonyl-C₁-C₄alkyl, C₁-C₆alkoxycarbonyl-C₁-C₄haloalkyl, C₁-C₆alkoxycarbonyl-benzyl, C₁-C₆alkenyloxycarbonyl-C₁-C₄alkyl, C₁-C₆alkynyloxycarbonyl-C₁-C₄alkyl, C₁-C₆alkylcarbonyloxy-C₁-C₄alkyl, C₁-C₆alkenylcarbonyloxy-C₁-C₄alkyl, C₁-C₆cycloalkylcarbonyloxy-C₁-C₄alkyl, benzoyloxy-C₁-C₄alkyl, C₁-C₆alkoxycarbonyloxy-C₁-C₄alkyl, C₁-C₆alkylaminocarbonyl-C₁-C₄alkyl, C₁-

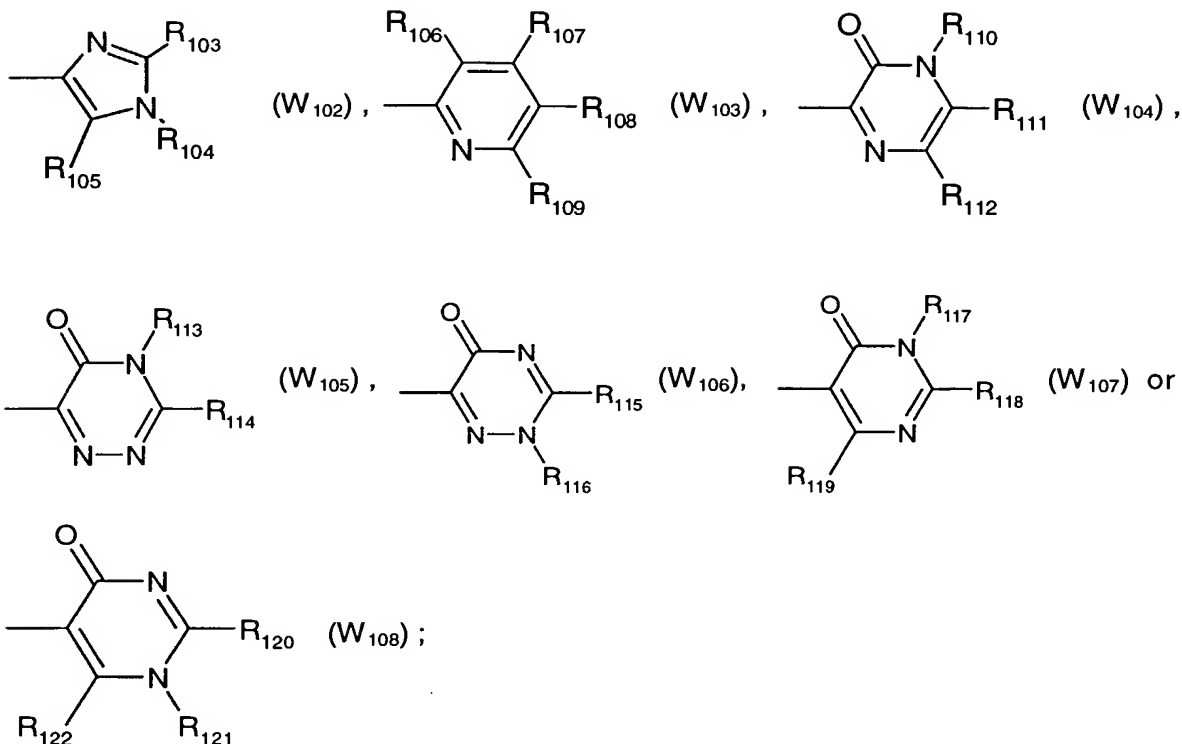
C₆alkylaminocarbonyl-benzyl, or C₁-C₄alkyl substituted by phenyl or by heterocyclyl, wherein the phenyl and heterocyclyl group may be substituted one or more times by halogen, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkenyl, C₁-C₆alkynyl, C₁-C₆haloalkenyl, C₁-C₆haloalkynyl, C₁-C₆cycloalkyl-C₁-C₄alkyl, C₁-C₆halocycloalkyl-C₁-C₄alkyl, cyano-C₁-C₁₂alkyl, C₁-C₆alkoxy-C₁-C₄alkyl, C₁-C₆alkylthio-C₁-C₄alkyl, C₁-C₆alkylsulfinyl-C₁-C₄alkyl, C₁-C₆alkylsulfonyl-C₁-C₄alkyl, hydroxy-C₁-C₁₂alkyl, C₁-C₆alkylcarbonyl-C₁-C₄alkyl, C₁-C₆alkoxycarbonyl-C₁-C₄alkyl, C₁-C₆alkoxycarbonyl-C₁-C₄haloalkyl, C₁-C₆alkylcarbonyloxy-C₁-C₄alkyl, C₁-C₆alkoxycarbonyloxy-C₁-C₄alkyl, C₁-C₄alkoxy-C₁-C₂alkoxy-C₁-C₂alkyl or by phenyl;

R₃ is hydrogen, C₁-C₁₂alkyl, C₁-C₁₂haloalkyl or unsubstituted or substituted phenyl;

R₄ is hydrogen or C₁-C₆alkyl;

W is a group





R₁₁ is hydrogen, C₁-C₃alkyl, halogen, C₁-C₃haloalkyl or cyano;

R₁₂ is C₁-C₃alkyl, C₁-C₃haloalkyl, C₁-C₃alkyl-S(O)_{n1}, C₁-C₃haloalkyl-S(O)_{n1} or cyano;
and

R₁₃ is C₁-C₃alkyl, C₁-C₃haloalkyl or amino; or

R₁₂ and R₁₁ or R₁₂ and R₁₃ together form a C₃- or C₄-alkylene bridge which may be substituted by halogen, C₁-C₃haloalkyl or by cyano;

R₁₄ is hydrogen, C₁-C₃alkyl, halogen, C₁-C₃haloalkyl or cyano; and

R₁₅ is C₁-C₃alkyl, C₁-C₃haloalkyl, C₁-C₃alkyl-S(O)_{n2}, C₁-C₃haloalkyl-S(O)_{n2} or cyano; or
R₁₅ and R₁₄ together form a C₃- or C₄-alkylene bridge which may be substituted by halogen, C₁-C₃haloalkyl or by cyano;

R₁₆ is hydrogen, C₁-C₃alkyl, halogen, C₁-C₃haloalkyl, C₁-C₃alkoxy, C₁-C₃haloalkoxy, C₁-C₃alkylthio, C₁-C₃alkylsulfinyl, C₁-C₃alkylsulfonyl or cyano;

n₁ and n₂ are 0, 1 or 2;

R₁₇ is hydrogen, C₁-C₃alkyl, halogen or cyano; and

R₁₈ is C₁-C₃alkyl, halogen, C₁-C₃haloalkyl, C₁-C₃alkylthio, C₁-C₃alkylsulfinyl, C₁-C₃alkylsulfonyl or cyano; or

R₁₈ and R₁₇ together form a C₃- or C₄-alkylene or C₃- or C₄-alkenylene bridge, both of which may be substituted by halogen, C₁-C₃alkyl or by C₁-C₃haloalkyl;

R₁₉ is hydrogen, halogen, C₁-C₃alkyl or amino; or

R₁₉ and R₁₈ together form a C₃- or C₄alkylene or C₃- or C₄-alkenylene bridge, both of which may be substituted by halogen, C₁-C₃alkyl or C₁-C₃haloalkyl;

R₂₀ and R₂₁ are each independently of the other hydrogen or C₁-C₄alkyl; or

R₂₀ and R₂₁ together are a group $\begin{array}{c} \text{R}_{051} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{R}_{052} \end{array}$;

R₀₅₁ and R₀₅₂ are each independently of the other C₁-C₄alkyl; or

R₀₅₁ and R₀₅₂ together form a C₄- or C₅-alkylene bridge;

R₀₅₁ and R₂₂ together form a C₃alkylene bridge;

R₂₂ is hydrogen or C₁-C₃alkyl; or

R₂₂ and R₂₀ or R₂₂ and R₂₁ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen or by -C(O)- and/or substituted by halogen, C₁-C₄alkyl, C₁-C₃haloalkyl, C₂-C₄alkenyl, C₁-C₃alkoxycarbonyl, C₁-C₃alkylcarbonyloxy, C₁-C₃alkylsulfonyloxy or by hydroxy;

R₂₃ is hydrogen, C₁-C₃alkyl or C₁-C₃haloalkyl; or

R₂₃ and R₂₄ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)-;

R₂₅ is hydrogen, halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, C₁-C₄alkylthio, C₁-C₄haloalkylthio, C₁-C₄alkylsulfinyl, C₁-C₄haloalkylsulfinyl, C₁-C₄alkylsulfonyl, C₁-C₄haloalkylsulfonyl or cyano; and

R₂₆ is hydrogen, C₁-C₄alkyl or C₁-C₄haloalkyl; or

R₂₆ and R₂₅ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen or by -C(O)- and/or substituted by halogen, C₁-C₄alkyl, C₁-C₃haloalkyl, C₂-C₄alkenyl, C₁-C₃alkoxycarbonyl, C₁-C₃alkylcarbonyloxy, C₁-C₃alkylsulfonyloxy or by hydroxy;

R₂₇ and R₂₈ are each independently of the other hydrogen or C₁-C₄alkyl; or

R₂₇ and R₂₈ together form a C₃-C₅alkylene bridge or a C₄alkenylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)-;

R₂₉ and R₃₀ are each independently of the other hydrogen or C₁-C₄alkyl; or

R₂₉ and R₃₀ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)-;

R₃₁ is hydrogen, C₁-C₄alkyl or C₁-C₄haloalkyl; and

R₃₂ is hydrogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkylthio, C₁-C₄alkylsulfinyl, C₁-C₄alkylsulfonyl, cyano or nitro; or

R₃₁ and R₃₂ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)-;

R₃₃ is hydrogen, C₁-C₃alkyl, halogen, C₁-C₃haloalkyl, C₁-C₃alkoxy, C₁-C₃haloalkoxy, C₁-C₃alkylthio, C₁-C₃alkylsulfinyl, C₁-C₃alkylsulfonyl, amino, C₁-C₃alkylamino, C₁-C₃alkylcarbonylamino, C₁-C₃haloalkylcarbonylamino or cyano;

R₃₄ is C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄alkylthio;

R₁₀₀ is hydrogen, halogen, nitro, amino, cyano, C₁-C₃alkyl, C₂- or C₃-alkenyl or C₂- or C₃-alkynyl;

R₁₀₁ is hydrogen, halogen, nitro, amino, cyano, hydroxy, mercapto, C₁-C₃alkyl, C₁-C₃haloalkyl, C₂- or C₃-alkenyl, C₂- or C₃-alkynyl, C₁-C₃alkoxy, C₁-C₃haloalkoxy, C₁-C₃alkylthio, C₁-C₃alkylsulfinyl, C₁-C₃alkylsulfonyl, C₁-C₃haloalkylthio, C₁-C₃haloalkylsulfinyl, C₁-C₃haloalkylsulfonyl, FS(O)₂-, ClS(O)₂-, C₁-C₆alkylsulfonyloxy, C₁-C₆haloalkylsulfonyloxy, C₁-C₃alkylcarbonyl, HC(O)-, HOC(O)-, ClC(O)-, FC(O)-, C₁-C₃alkoxycarbonyl, H₂NC(O)- or H₂NC(S)-;

R₁₀₂ is hydrogen, C₁-C₆alkyl, C₃-C₆alkenyl, C₃-C₆alkynyl, C₃-C₆cycloalkyl, C₁-C₆haloalkyl, C₁-C₃alkylsulfonyl, or C₁-C₆alkyl which may be substituted by cyano, HO-, HOC(O)-, C₁-C₃alkoxycarbonyl or by HC(O)-; or,

when W is a group W₁₀₀,

R₁₀₂ and R₁₀₁ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen;

R₁₀₃ is as defined for R₁₀₁;

R₁₀₄ is as defined for R₁₀₂;

R₁₀₅ is as defined for R₁₀₀;

R₁₀₆ is hydrogen, halogen, amino, nitro, hydroxy, C₁-C₃alkyl or C₁-C₃alkoxy;

R₁₀₇ is hydrogen, halogen, amino, hydroxy, C₁-C₃alkyl, C₁-C₃haloalkyl, HC(O)-, HOC(O)-, hydroxy-C₁-C₃alkyl, C₁-C₃alkoxy or C₁-C₃haloalkoxy; and

R₁₀₈ is hydrogen, halogen, nitro, amino, cyano, HC(O)-, HOC(O)-, H₂NC(O)-, H₂NC(S)-, hydroxy, HS-, C₁-C₃alkyl, C₁-C₃haloalkyl, C₂- or C₃-alkenyl, C₁-C₃alkoxy, C₁-C₃haloalkoxy, C₁-C₃alkylcarbonyl, C₁-C₃alkoxycarbonyl, C₁-C₃alkylthio, C₁-C₃haloalkylthio, C₁-C₃alkylsulfinyl, C₁-C₃haloalkylsulfinyl, C₁-C₃alkylsulfonyl, C₁-C₃haloalkylsulfonyl, C₁-C₃alkylsulfonyloxy or C₁-C₃haloalkylsulfonyloxy;

R₁₀₉ is as defined for R₁₀₇;

R₁₀₇ and R₁₀₈ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen;

R₁₀₈ and R₁₀₉ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen;

R₁₁₀ is hydrogen, C₁-C₃alkyl, C₁-C₃haloalkyl, C₃-C₄alkenyl or C₃-C₄alkynyl;

R₁₁₁ is as defined for R₁₀₈;

R₁₁₂ is as defined for R₁₀₉;

R₁₁₁ and R₁₁₂ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen;

R₁₁₀ and R₁₁₁ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein a CH₂ group is bonded to the N atom of the pyrazinone;

R₁₁₃ is as defined for R₁₁₀;

R₁₁₄ is as defined for R₁₀₈;

R₁₁₃ and R₁₁₄ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein a CH₂ group is bonded to the N atom of the triazinone;

R₁₁₅ is as defined for R₁₀₈;

R₁₁₆ is as defined for R₁₁₀;

R₁₁₅ and R₁₁₆ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein a CH₂ group is bonded to the N atom of the triazinone;

R₁₁₇ is as defined for R₁₁₀;

R₁₁₈ is as defined for R₁₀₈;

R₁₁₉ is as defined for R₁₀₆;

R₁₁₇ and R₁₁₈ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein a CH₂ group is bonded to the N atom of the pyrimidinone;

R₁₂₀ is as defined for R₁₀₈;

R₁₂₁ is as defined for R₁₁₀;

R₁₂₂ is as defined for R₁₀₆;

R₁₂₁ and R₁₂₀ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein a CH₂ group is bonded to the N atom of the pyrimidinone;

X₁, X₂, X₃, X₄, X₅, X₆, X₇, X₈, X₉, X₁₀, X₁₁, X₁₂ or X₁₃ are each independently of the others oxygen or sulfur; and

Y₁ is oxygen or sulfur.

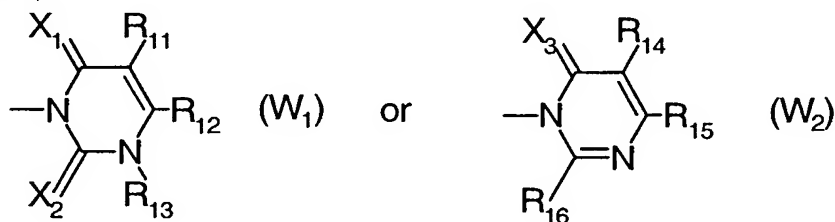
Preference is also given to compounds of formula I wherein R₁ is hydrogen or fluorine.

In further preferred compounds of formula I, R_2 is hydrogen, methyl, ethyl, n-propyl, isopropyl, 2-methylpropyl, 3-methylpropyl, n-butyl, 2-butyl, 3-methyl-but-1-yl, 2-pentyl, 3-pentyl, allyl, 1-methyl-prop-2-en-1-yl, 2-methyl-prop-2-en-1-yl, 3-methyl-prop-2-en-1-yl, 2-buten-1-yl, 3-buten-1-yl, 1-buten-3-yl, 4-penten-1-yl, propargyl, 1-butyne-3-yl, 2,2,2-trifluoroethyl, 2-chloroethyl, 3-fluoroprop-1-yl, 3-chloroprop-1-yl, 3-chloro-2-methylprop-1-yl, 4-chlorobut-1-yl, 1-chloro-prop-1-en-3-yl, 2-chloro-prop-1-en-3-yl, 3-chloro-but-2-en-1-yl, 5-chloropentyl, 2-bromo-prop-1-en-3-yl, 6,6-dimethyl-hept-2-en-4-yn-1-yl, dimethylethylsilylmethyl, trimethylsilylmethyl-prop-2-en-1-yl, cyclopropylmethyl, dichlorocyclopropylmethyl, cyanoethyl, methoxyethyl, ethoxyethyl, ethylthioethyl, 2,2-dimethoxyethyl, 3,3-dimethoxypropyl, ethylcarbonylmethyl, tert.-butylcarbonylmethyl, cyclopropylcarbonylmethyl, oxiranylmethyl, methoxycarbonylmethyl, ethoxycarbonylmethyl, 1-(methoxycarbonyl)-ethyl, 1-(ethoxycarbonyl)-ethyl, 1-(methoxycarbonyl)-prop-1-yl, benzyl or 2-methoxybenzyl; R_3 is hydrogen, methyl, ethyl, n-propyl or n-butyl; and R_4 is hydrogen or methyl.

In a selected group of compounds of formula I, W is a group W_1 to W_{21} . Of those compounds, special preference is given to those wherein W is a group W_1 , W_2 , W_4 , W_5 , W_7 , W_{11} , W_{12} , W_{14} , W_{15} , W_{18} or W_{21} . Of those compounds, very special preference is given to those wherein W is a group W_1 , W_2 , W_4 , W_5 , W_7 or W_{11} .

In a further selected group of compounds of formula I, W is a group W_3 , W_6 , W_8 , W_9 , W_{10} , W_{13} , W_{16} , W_{17} or W_{19} .

In a preferred group of compounds of formula I, W is a group W_1 or W_2

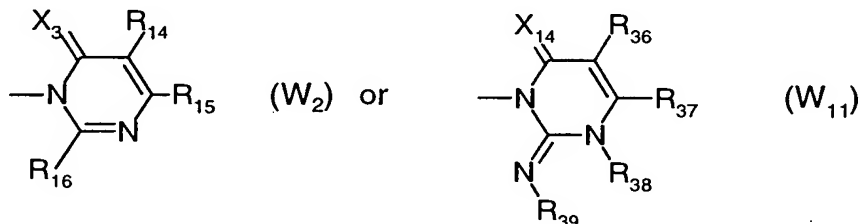


wherein R_{11} , R_{12} , R_{13} , R_{14} , R_{15} , R_{16} , X_1 , X_2 and X_3 are as defined for formula I. Of those compounds, special preference is given to those wherein X_1 and X_3 are oxygen; R_{11} and R_{14} are hydrogen, chlorine or methyl; R_{12} and R_{15} are methyl, ethyl, chlorodifluoromethyl, trifluoromethyl, pentafluoroethyl or cyano; R_{13} is methyl, fluoromethyl, propargyl or amino; and R_{16} is chlorine, methoxy, fluoromethoxy or methylthio.

Of those compounds, very special preference is given to those wherein X_1 , X_2 and X_3 are oxygen; R_{11} and R_{14} are hydrogen or methyl; R_{12} and R_{15} are trifluoromethyl,

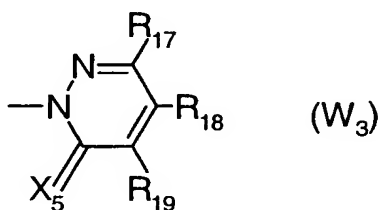
pentafluoroethyl or cyano; R_{13} is methyl or amino; and R_{16} is chlorine or methoxy. Of those compounds, preference is given more especially to those wherein W is a group W_1 ; R_{11} is hydrogen; R_{12} is trifluoromethyl; and R_{13} is methyl, fluoromethyl or amino.

In a further preferred group of compounds of formula I, W is a group W_2 or W_{11}



wherein R_{14} , R_{15} , R_{36} , R_{37} , R_{38} , R_{39} , X_3 and X_{14} are as defined for formula I; and R_{16} is amino, C_1 - C_3 alkylamino, di(C_1 - C_3 alkyl)amino, allylamino or propargylamino. Of those compounds, special preference is given to those wherein X_3 and X_{14} are oxygen; R_{14} and R_{36} are hydrogen, chlorine or methyl; R_{15} and R_{37} are methyl, ethyl, chlorodifluoromethyl, trifluoromethyl, pentafluoroethyl or cyano; R_{16} is amino or methylamino; and R_{39} and R_{38} together form an unsubstituted or methyl-substituted C_2 alkylene or C_2 alkenylene bridge. Of those compounds, very special preference is given to those wherein R_{15} and R_{37} are trifluoromethyl.

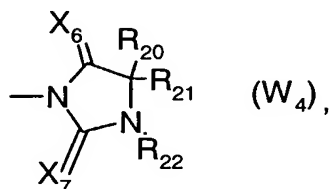
In another preferred group of compounds of formula I, W is a group W_3



wherein R_{17} , R_{18} , R_{19} and X_5 are as defined for formula I. Special preference is given especially to those wherein R_{17} is hydrogen or C_1 - C_3 alkyl; R_{18} is trifluoromethyl or methylsulfonyl; R_{19} is hydrogen, C_1 - C_3 alkyl or amino; and X_5 is oxygen. Of those compounds, very special preference is given to those wherein R_{17} is hydrogen; and R_{19} is methyl or amino.

Special preference is given to compounds of formula I wherein W is a group W_3 ; R_{17} and R_{19} are each independently of the other hydrogen or methyl; and R_{18} is trifluoromethyl, pentafluoroethyl or cyano. Very special preference is given especially to those wherein R_{17} is hydrogen; R_{18} is trifluoromethyl; and R_{19} is hydrogen or methyl.

Preference is also given to compounds of formula I wherein W is the group W₄



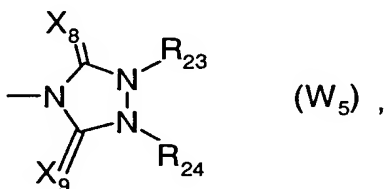
R₂₀, R₂₁ and R₂₂ are as defined for formula I, and X₆ and X₇ are oxygen. Of those compounds, special preference is given especially to those wherein R₂₁ and R₂₂ together form a C₃- or C₄-alkylene bridge which is substituted once or twice by fluorine or chlorine or once by hydroxy or is interrupted by a keto group. Special preference is also given to those

compounds wherein R₂₀ and R₂₁ together are a group ; R₀₅₁ is hydrogen; and

R₀₅₂ and R₂₂ together form a C₃alkylene bridge.

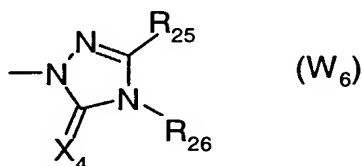
In an especially preferred group of compounds, W is a group W₄ wherein R₂₀ is hydrogen; and R₂₁ and R₂₂ together form a C₄alkylene group which is unsubstituted or substituted once or twice by fluorine or chlorine.

Preference is also given to compounds of formula I wherein W is the group W₅



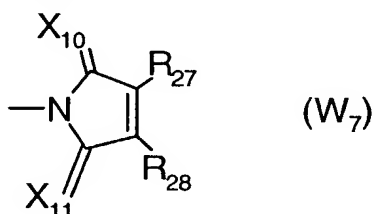
R₂₃ and R₂₄ are as defined for formula I; and X₈ and/or X₉ are oxygen. Of those compounds, special preference is given to those wherein R₂₃ and R₂₄ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen. Very special preference is given to those wherein R₂₃ and R₂₄ together form a C₃- or C₄-alkylene bridge.

In another preferred group of compounds of formula I, W is a group W₆



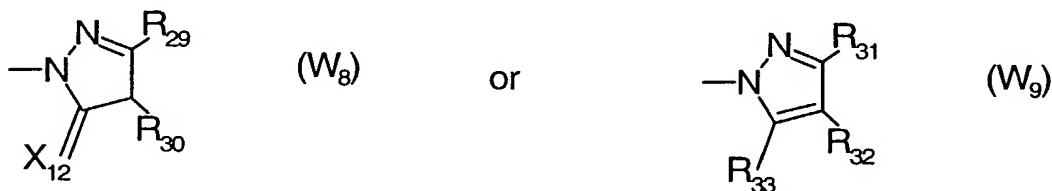
wherein R_{25} and R_{26} are as defined for formula I; and X_4 is oxygen. Of those compounds, special preference is given to those wherein R_{25} and R_{26} together form a C_4 alkylene bridge. In another especially preferred group, W is a group W_6 ; R_{25} is methyl, ethyl or trifluoromethyl; and R_{26} is methyl or difluoromethyl. Of those compounds, very special preference is given to those wherein X_4 is oxygen.

In a further preferred group of compounds of formula I, W is a group W_7



wherein R_{27} and R_{28} are as defined for formula I; and X_{10} and X_{11} are oxygen. Of those compounds, special preference is given to those wherein R_{27} and R_{28} together form a C_4 alkylene bridge. Special preference is likewise given to those compounds wherein R_{27} is methyl and R_{28} is C_1 - C_3 alkyl.

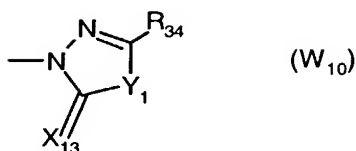
In other preferred groups of compounds of formula I, W is a group W_8 or W_9



wherein R_{29} , R_{30} , R_{31} , R_{32} and R_{33} are as defined for formula I; and X_{12} is oxygen. Of those compounds, special preference is given to those wherein R_{29} and R_{30} together and R_{31} and R_{32} together form, in each case, a C_4 alkylene bridge. Of those groups, very special preference is given especially to those wherein W is a group W_9 and R_{33} is chlorine or bromine.

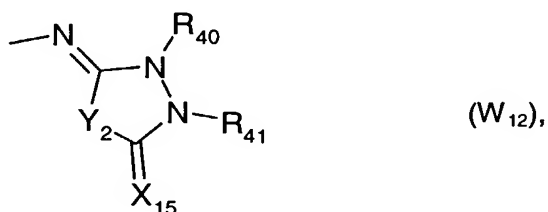
In a further group of preferred compounds, W is a group W_9 wherein R_{31} is hydrogen, chlorine, methyl or trifluoromethyl; R_{32} is methyl, trifluoromethyl, methylthio, methylsulfinyl, methylsulfonyl, cyano or nitro; and R_{33} is chlorine, amino, methylamino or ethylamino.

In another preferred group of compounds of formula I, W is a group W_{10}



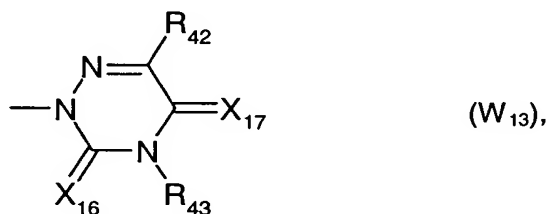
wherein X₁₃ is oxygen; and R₃₄ and Y₁ are as defined for formula I. Of those compounds, special preference is given to those wherein R₃₄ is tert-butyl or trifluoromethyl.

Preference is likewise given to compounds of formula I wherein W is a group W₁₂



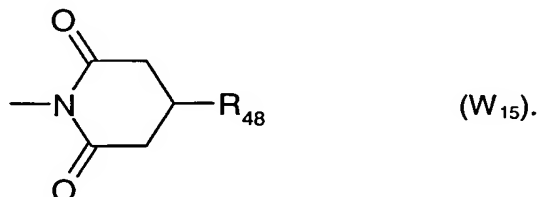
X₁₅ is oxygen; Y₂ is sulfur; R₄₀ is methyl or ethyl; and R₄₁ is methyl, ethyl or difluoromethyl; or R₄₀ and R₄₁ together form a -(CH₂)₃-, -CH₂CH(CH₃)CH₂-, -(CH₂)₄-, -CH₂CH₂OCH₂- or -CH₂CH₂OCH₂CH₂- bridge.

In a further preferred group of compounds of formula I, W is a group W₁₃



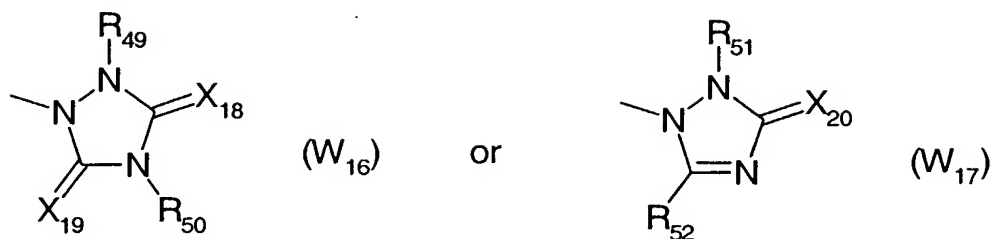
R₄₂ is hydrogen or cyano; R₄₃ is methyl; and X₁₆ and X₁₇ are oxygen.

In a further preferred group of compounds of formula I, W is a group W₁₅



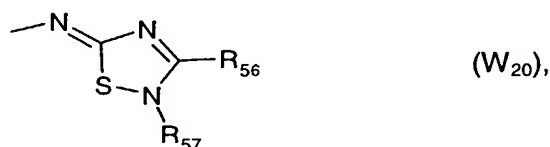
Of those compounds, special preference is given to those wherein R₄₈ is trifluoromethyl.

Preference is also given to compounds of formula I wherein W is a group W₁₆ or W₁₇



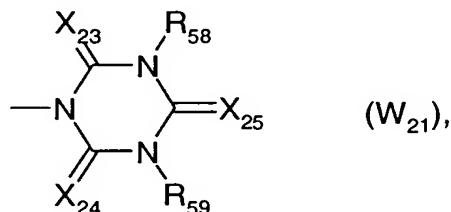
X₁₈ and X₂₀ are oxygen; R₄₉ is methyl; R₅₀ is methyl or difluoromethyl; and R₅₂ is chlorine or methyl.

Preference is also given to compounds of formula I wherein W is a group W₂₀



and R₅₆ and R₅₇ together form a -SCH₂CH₂-, -SCH(CH₃)CH₂-, -SC(CH₃)₂CH₂-, -SCH₂CH₂CH₂-, -(CH₂)₃-, -CH₂CH(CH₃)CH₂- or -CH₂C(CH₃)₂CH₂- bridge.

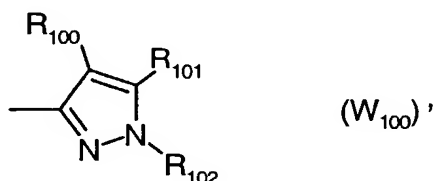
In a further preferred group of compounds of formula I, W is a group W₂₁



R₅₈ is methyl or amino; R₅₉ is methyl; and X₂₃ and X₂₄ are oxygen.

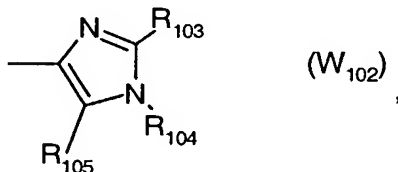
In another selected group of compounds of formula I, W is a group W₁₀₀, W₁₀₁, W₁₀₂, W₁₀₃, W₁₀₄, W₁₀₅, W₁₀₆, W₁₀₇, W₁₀₈ or W₁₀₉, especially the group W₁₀₀.

Very special preference is given to those compounds of formula I wherein W is a group W₁₀₀



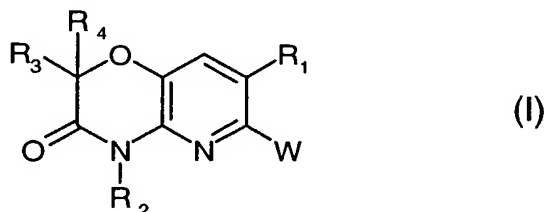
R₁₀₀ is methyl, chlorine or bromine; R₁₀₁ is chlorine, bromine, trifluoromethyl, difluoromethoxy, methylsulfonyl, ethylsulfonyl or cyano; and R₁₀₂ is methyl or ethyl; or R₁₀₂ and R₁₀₁ together form a C₄alkylene bridge.

Preference is also given to compounds of formula I wherein W is a group W₁₀₂

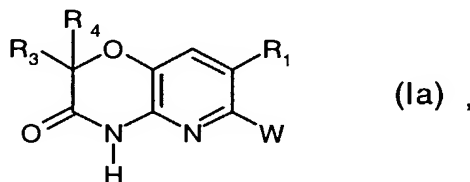


R₁₀₃ is methyl, ethyl or trifluoromethyl; and R₁₀₄ is methyl, ethyl or difluoromethyl; or R₁₀₄ and R₁₀₃ together form a C₄alkenylene bridge; and R₁₀₅ is methyl, chlorine or bromine.

The process according to the invention for the preparation of compounds of formula I according to variant a) and Reaction Scheme 1a is carried out analogously to known processes, as described, for example, in WO 98/42698, and comprises, for the preparation of those compounds of formula I



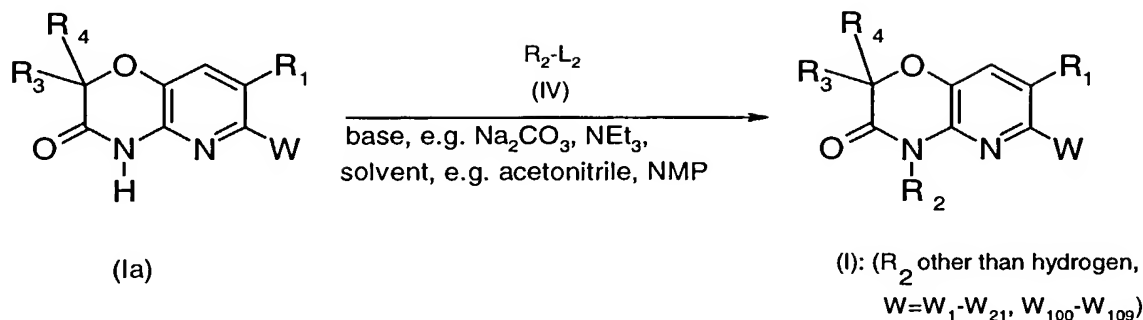
wherein R₁, R₂, R₃, R₄ and W are as defined for formula I with the exception of R₂ as hydrogen, reacting a compound of formula Ia



wherein R₁, R₃, R₄ and W are as defined, with a suitable alkylating reagent of formula IV

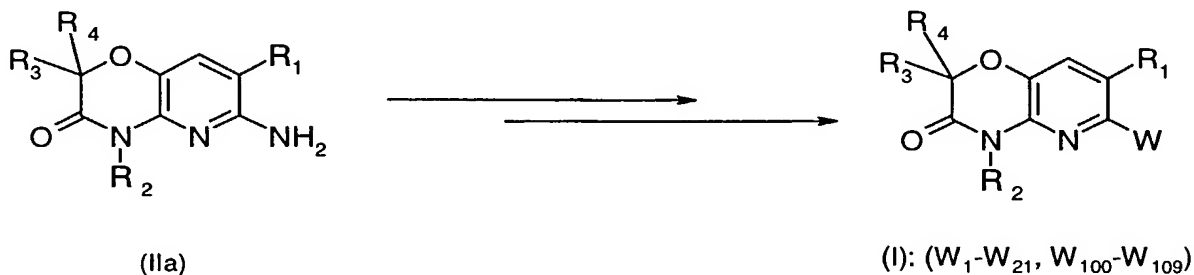


wherein R₂ is as defined for formula I with the exception of R₂ as hydrogen, and L₂ is a leaving group, for example halogen, especially chlorine, bromine or iodine, or a sulfonate, especially CH₃S(O)₂O- (mesyloxy) or p-tolyl-S(O)₂O- (tosyloxy), in the presence of a base and, optionally, one or more catalysts preferably in an inert diluent at temperatures of from -20° to 250°C, preferably from 20°C to the boiling point of the solvent or alkylating agent used, and at normal pressure or optionally under a slightly elevated pressure.

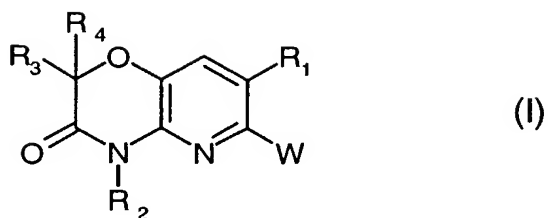
Reaction Scheme 1a:

Bases that are suitable for that alkylating reaction are, for example, alkali or alkaline earth metal hydrides, especially sodium hydride; alkali or alkaline earth metal carbonates, especially sodium hydrogen carbonate or sodium or potassium carbonate; trialkylamines, especially triethylamine or ethyl-diisopropylamine; aromatic amines, especially pyridine or N,N-dimethylaminopyridine; or caesium fluoride. Suitable catalysts are, for example, crown ethers, especially 15-crown-5 or 18-crown-6; alkali metal halides, especially sodium or potassium iodide; or copper(I) iodide. Suitable diluents are, for example, aromatic or heteroaromatic hydrocarbons, for example toluene, one of the xylene isomers, or 5-ethyl-2-methylpyridine; ketones, especially acetone or methyl ethyl ketone; ethers, especially tetrahydrofuran (THF), dimethoxyethane or diethoxymethane; esters, especially ethyl acetate; nitriles, especially acetonitrile; amides, especially N,N-dimethylformamide (DMF) or N-methylpyrrolidone (NMP); or sulfoxides, especially dimethyl sulfoxide.

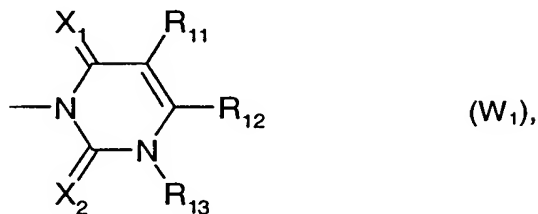
The process according to the invention for the preparation of compounds of formula I according to variant b) and Reaction Scheme 1b

Reaction Scheme 1b:

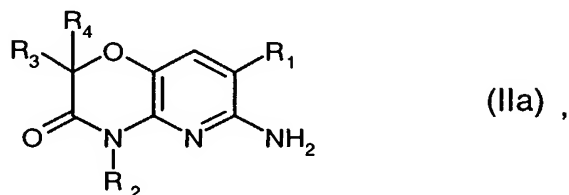
is carried out analogously to known processes, as described, for example, in WO 99/52892, WO 99/52893 and WO 98/27083, and comprises, for the preparation of those compounds of formula I



wherein R_1 , R_2 , R_3 and R_4 are as defined for formula I and W is a group W_1



wherein R_{11} , R_{12} , R_{13} , X_1 and X_2 are as defined for formula I, reacting a compound of formula IIa

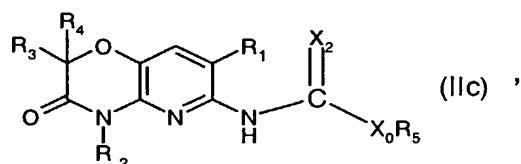


wherein R_1 , R_2 , R_3 and R_4 are as defined, either

1), according to route a) in Reaction Scheme 1, with a compound of formula VI



wherein X_2 is as defined for formula I, X_0 is oxygen, sulfur or amino, and R_5 is C_1 - C_4 alkyl, to yield the compound of formula IIc



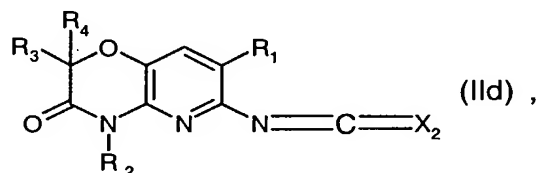
wherein R_1 , R_2 , R_3 , R_4 , R_5 , X_0 and X_2 are as defined, or, as a variant thereof and in cases where X_0 in the compound of formula IIc is sulfur, first of all 1) carrying out a reaction with the reagent of formula XIn



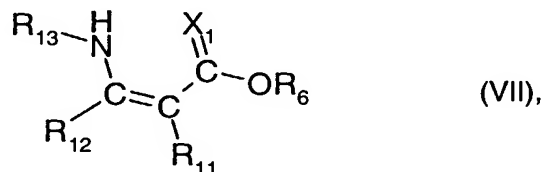
and then 2) with the alkylating reagent of formula IXb



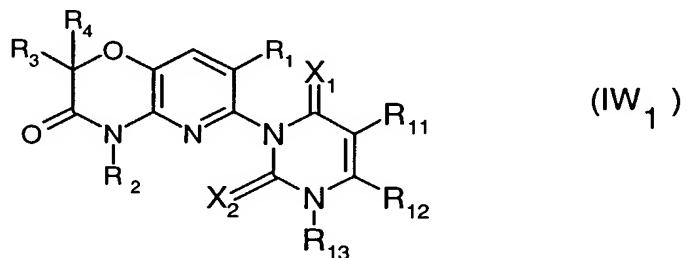
to yield the compound of formula IIc, the substituents X_2 and R_5 in the reagents of formulae XIa and IXb being as defined and L_1 being a leaving group, for example halogen, especially chlorine, bromine or iodine, or sulfonate, especially mesyloxy or tosyloxy, or 2), according to route b) in Reaction Scheme 1, carrying out treatment with (thio-)phosgene or oxalyl chloride to yield the compound of formula IId



wherein R_1 , R_2 , R_3 , R_4 and X_2 are as defined, and then, according to route c) in Reaction Scheme 1, condensing and cyclising the resulting compounds of formulae IIc and IId with an enamine of formula VII



wherein R_{11} , R_{12} and R_{13} are as defined, X_1 is oxygen or sulfur, and R_6 is C_1 - C_4 alkyl, in the presence of from 0.01 to 1.5 equivalents of a suitable base, for example an alkali metal hydroxide or hydride, e.g. sodium hydroxide or sodium hydride, or an alcoholate, e.g. sodium ethanolate or potassium tert-butanolate, in an inert solvent, for example an aromatic hydrocarbon, e.g. toluene or one of the xylene isomers, a nitrile, e.g. acetonitrile, or an amide, e.g. DMF or NMP (see also Example P4), to form the compound of formula IW₁

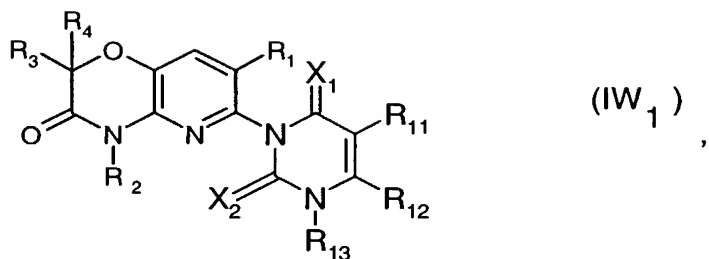


wherein R_1 , R_2 , R_3 , R_4 , R_{11} , R_{12} , R_{13} , X_1 and X_2 are as defined, and

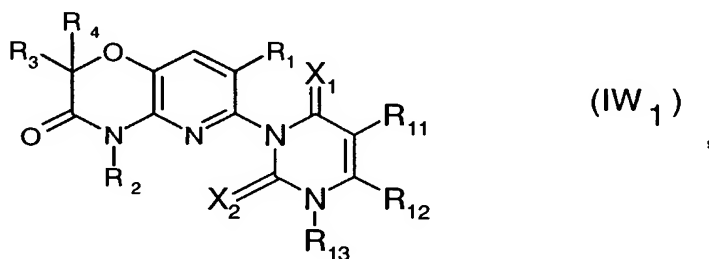
3) optionally, further functionalising those compounds according to the definition of R_1 , R_2 , R_{11} , R_{13} , X_1 and X_2 for formula I according to standard methods (Reaction Scheme 1).

Examples of such standard methods for further functionalisation are:

aa) thionation of compounds of formula IW₁

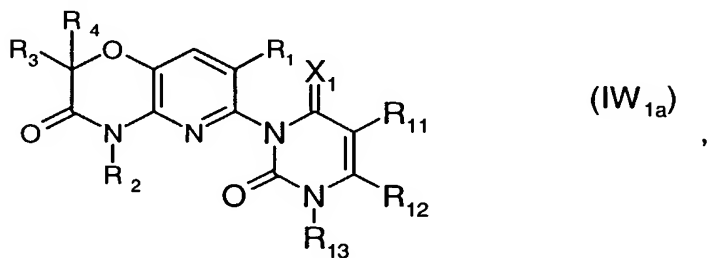


wherein R₁, R₂, R₃, R₄, R₁₁, R₁₂ and R₁₃ are as defined for formula I and X₁ and/or X₂ are oxygen, with the aid of a thionating reagent, for example Lawesson's reagent or P₂S₅ (phosphorus pentasulfide), to form the compound of formula IW₁



wherein R₁, R₂, R₃, R₄, R₁₁, R₁₂ and R₁₃ are as defined and X₁ and/or X₂ are sulfur (Reaction Scheme 1), or when X₂ is oxygen,

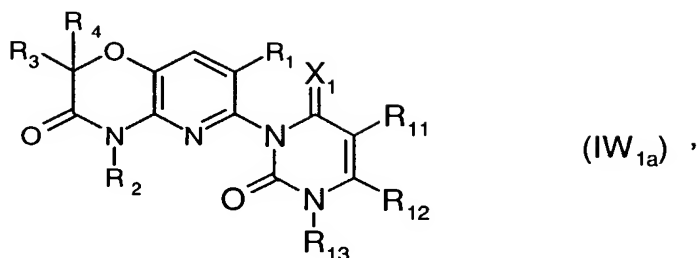
ab) alkylation of compounds of formula IW_{1a}



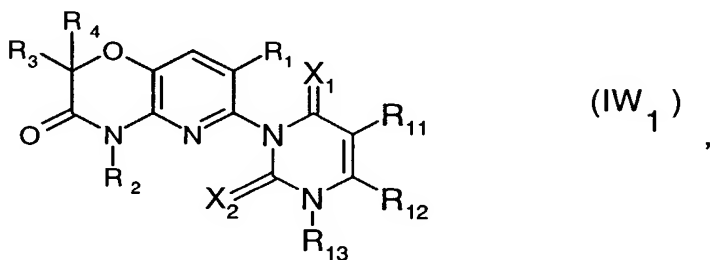
wherein R₁, R₂, R₃, R₄, R₁₁, R₁₂ and X₁ are as defined for formula I and R₁₃ is hydrogen, in the presence of a base, for example an alkali metal carbonate, e.g. potassium carbonate or sodium hydrogen carbonate, using an alkylating reagent of formula IX



wherein R₁₃ is as defined for formula I with the exception of R₁₃ as hydrogen and amino, and L₁ is a leaving group, for example halogen, especially chlorine, bromine or iodine, or a sulfonate, especially mesyloxy or tosyloxy, to form the compound of formula IW_{1a}



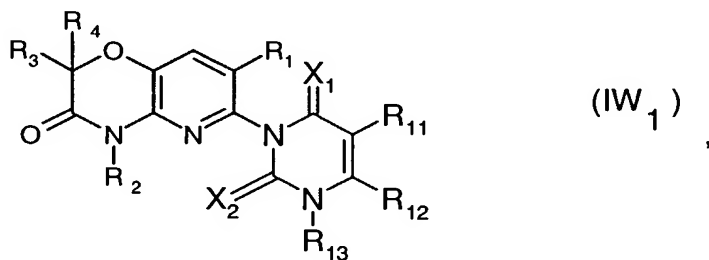
wherein R₁, R₂, R₃, R₄, R₁₁, R₁₂, R₁₃ and X₁ are as defined, (Reaction Scheme 1), or
ac) alkylation of compounds of formula IW₁



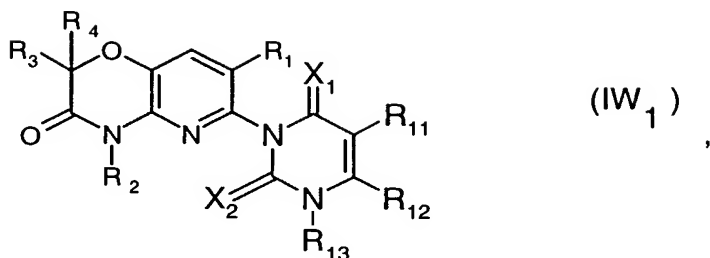
wherein R₁, R₃, R₄, R₁₁, R₁₂, R₁₃, X₁ and X₂ are as defined for formula I with the exception of R₁₃ as amino, and R₂ is hydrogen, in the presence of a base, for example an alkali metal carbonate, especially potassium carbonate, and a catalyst, for example 18-crown-6 or potassium iodide, using an alkylating reagent of formula IV



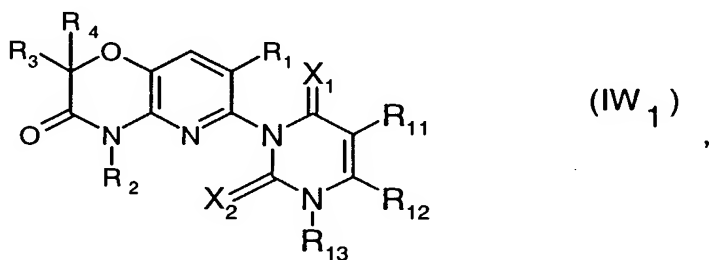
wherein R₂ is as defined for formula I with the exception of R₂ as hydrogen, and L₂ is a leaving group, for example halogen, especially chlorine, bromine or iodine, or a sulfonate, especially mesyloxy or tosyloxy, to form the compound of formula IW₁



wherein R₁, R₂, R₃, R₄, R₁₁, R₁₂, R₁₃, X₁ and X₂ are as defined (Reaction Scheme 1), with the proviso that, when X₂ in the compound of formula IW₁ is sulfur, R₁₃ must be other than hydrogen (S-alkylation), or
ad) amination of compounds of formula IW₁

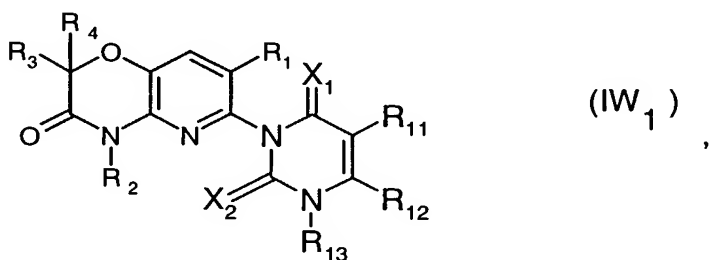


wherein R₁, R₂, R₃, R₄, R₁₁, R₁₂, X₁ and X₂ are as defined for formula I and R₁₃ is hydrogen, using an electrophilic aminating reagent, for example 1-aminooxy-2,4-dinitrobenzene, in analogous manner to that described, for example, in WO 96/36614, to form the compound of formula IW₁

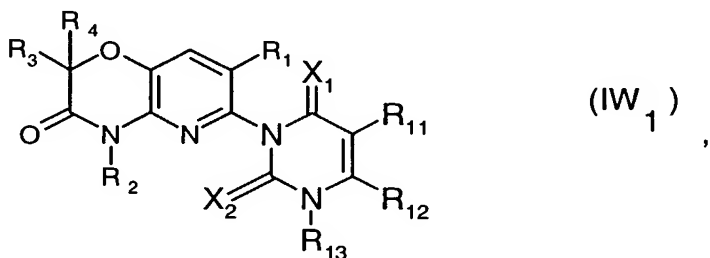


wherein R₁, R₂, R₃, R₄, R₁₁, R₁₂, X₁ and X₂ are as defined and R₁₃ is amino (Reaction Scheme 1), or

ae) halogenation of compounds of formula IW₁

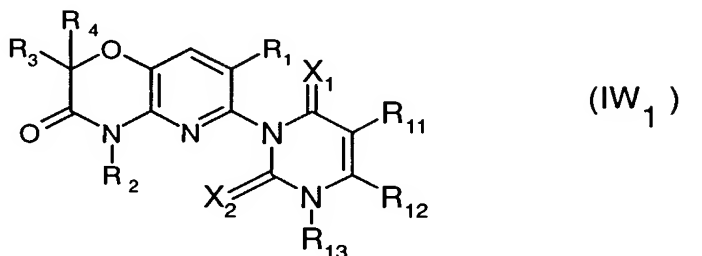


wherein R₂, R₃, R₄, R₁₂, R₁₃, X₁ and X₂ are as defined for formula I and R₁ and/or R₁₁ are hydrogen, using a halogenating reagent, for example chlorine, bromine or iodine, to form the compound of formula IW₁

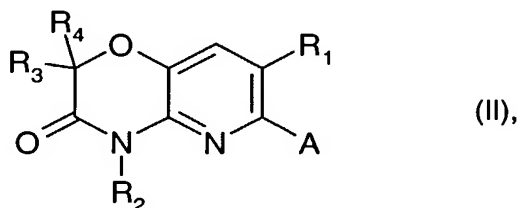


wherein R_2 , R_3 , R_4 , R_{12} , R_{13} , X_1 and X_2 are as defined and R_1 and/or R_{11} are halogen (Reaction Scheme 1), or

af) fluorination of compounds of formula IW_1

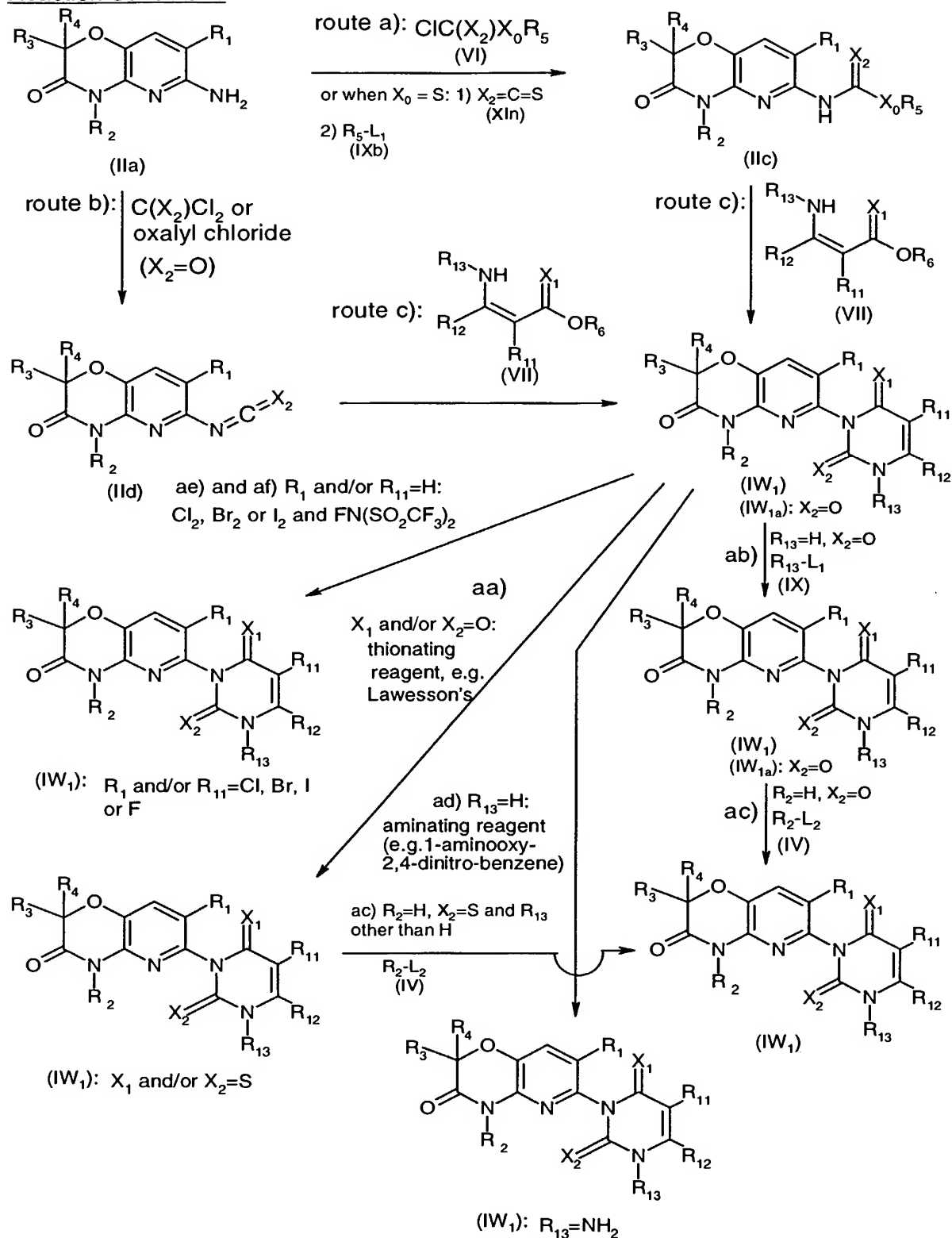


wherein R_2 , R_3 , R_4 , R_{12} , R_{13} , X_1 and X_2 are as defined for formula I and R_1 and/or R_{11} are hydrogen, using an electrophilic fluorinating reagent, for example $FN(SO_2CF_3)_2$ or SelectfluorTM (= 1-chloromethyl-4-fluoro-1,4-diazabicyclo[2.2.2]octane bis(tetrafluoroborate); Manufacturer: Air Products European Technology Group, England), preferably after activation by means of a metallation reaction, for example using n-butyllithium, sec-butyllithium or lithium diisopropylamide (LDA), and advantageously with the aid of an ortho-directing group, for example a uracil radical in a compound of formula IW_1 or a group A in a compound of formula II

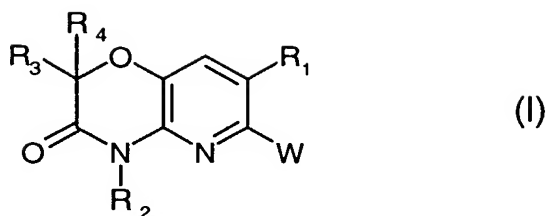


wherein R_2 , R_3 and R_4 are as defined for formula I, R_1 is hydrogen, and A is, for example, a group $-NHC(X_2)R_5$ or $-NHC(X_2)X_0R_5$, wherein X_2 is oxygen or sulfur, X_0 is oxygen, sulfur or amino, and R_5 is C_1 - C_6 alkyl or phenyl, to form the compound of formula IW_1 wherein R_2 , R_3 , R_4 , R_{12} , R_{13} , X_1 and X_2 are as defined and R_1 and/or R_{11} are fluorine, or to form the compound of formula II wherein R_2 , R_3 , R_4 and A are as defined and R_1 is fluorine (Reaction Scheme 1).

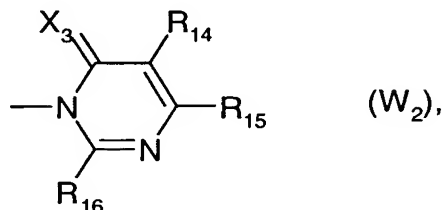
The fluorination may advantageously be carried out in an organic solvent, for example a cyclic ether, e.g. tetrahydrofuran, in the presence of an auxiliary base, for example tetramethylethylenediamine, and a further polar, aprotic solvent.

Reaction Scheme 1:

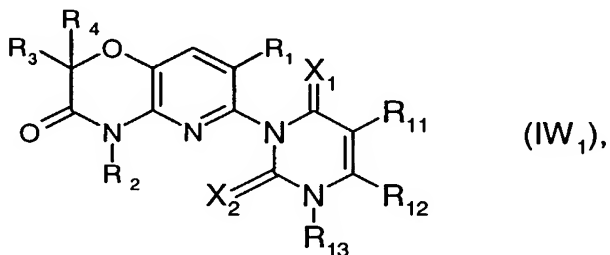
The process according to the invention for the preparation of compounds of formula I is carried out according to variant b) and Reaction Scheme 1b) and comprises, for the preparation of those compounds of formula I



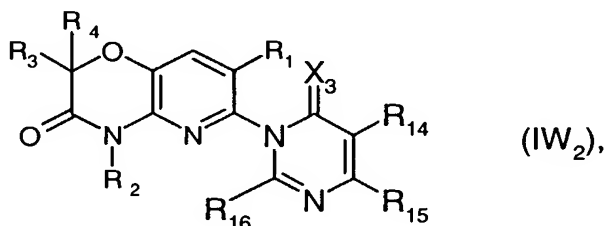
wherein R_1 , R_2 , R_3 and R_4 are as defined for formula I and W is a group W_2



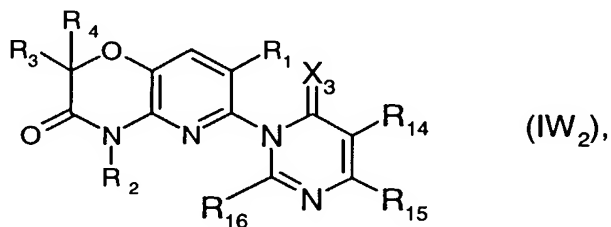
wherein R_{14} , R_{15} and X_3 are as defined for formula I and R_{16} is hydrogen, C_1 - C_3 alkyl, C_1 - C_3 haloalkyl, halogen, C_1 - C_3 alkoxy, C_1 - C_3 haloalkoxy, mercapto, C_1 - C_3 alkylthio, C_1 - C_3 alkylsulfanyl, C_1 - C_3 alkylsulfonyl, allylthio, propargylthio, amino, C_1 - C_3 alkylamino, di(C_1 - C_3 alkyl)amino, allylamino, propargylamino or cyano, treating a compound of formula IW_1



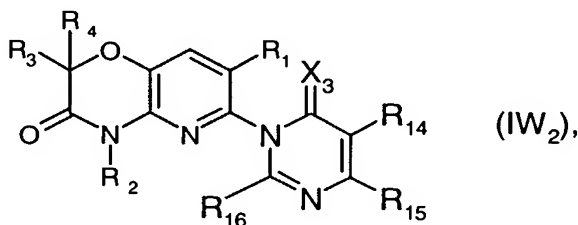
wherein R_1 , R_2 , R_3 , R_4 , R_{11} , R_{12} , X_1 and X_2 are as defined for formula I and R_{13} is hydrogen, either, according to route f) in Reaction Scheme 2, with an alkylating reagent, for example R_{13} - L_1 of formula IX, wherein R_{13} is C_1 - C_3 alkyl, C_1 - C_3 haloalkyl, allyl or propargyl, and L_1 is a leaving group, for example halogen, especially chlorine, bromine or iodine, or a sulfonate, especially mesyloxy, or with a dialkyl sulfate of formula $(R_2O)_2SO_2$, wherein R_2 is as defined for formula I with the exception of R_2 as hydrogen, or with a Meerwein's salt ($R_3O \cdot BF_4$), wherein R is preferably methyl or ethyl, or a freonising reagent, for example CHF_2Cl or $BrCH_2F$, and thereby effecting direct conversion into the compound of formula IW_2



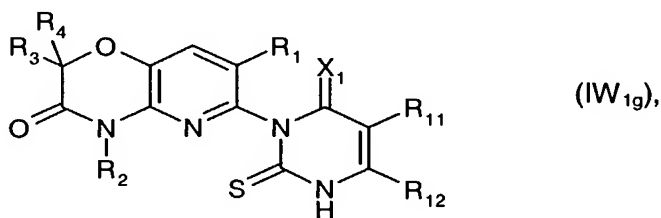
wherein R_1 , R_2 , R_3 and R_4 are as defined, R_{14} , R_{15} and X_3 are as defined for R_{11} , R_{12} and X_1 , respectively, and R_{16} is C_1 - C_3 alkoxy, C_1 - C_3 haloalkoxy, C_1 - C_3 alkylthio, allylthio or propargylthio, or, according to route d) in Reaction Scheme 2, first of all obtaining, using a halogenating reagent, for example phosphorus oxychloride, the compound of formula IW_2



wherein R_1 , R_2 , R_3 and R_4 are as defined, R_{14} , R_{15} and X_3 are as defined for R_{11} , R_{12} and X_1 , respectively, and R_{16} is halogen, especially chlorine, and then converting that compound *via* a nucleophilic substitution reaction, for example with a C_1 - C_3 alcoholate, a C_1 - C_3 alkylthiolate or an alkali metal cyanide, into the compound of formula IW_2



wherein R_1 , R_2 , R_3 , R_4 , R_{14} , R_{15} and X_3 are as defined and R_{16} is C_1 - C_3 alkoxy, C_1 - C_3 alkylthio or cyano, or, when X_2 in the compound of formula IW_1 is oxygen, first of all converting that compound, according to route e) in Reaction Scheme 2, using a thionating reagent, for example phosphorus pentasulfide (P_2S_5), into the compound of formula IW_{1g}



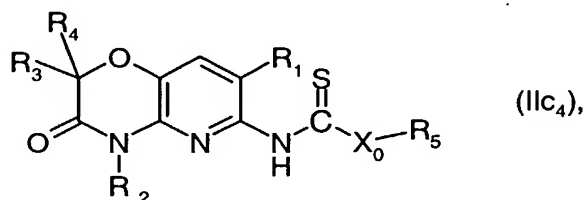
wherein R_1 , R_2 , R_3 , R_4 , R_{11} , R_{12} and X_1 are as defined, and then treating that compound with an alkylating reagent of formula



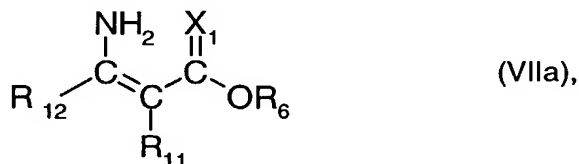
wherein R_{13} is C_1 - C_3 alkyl, C_1 - C_3 haloalkyl, allyl or propargyl, and L_1 is a leaving group, for example halogen, especially chlorine, bromine or iodine, or sulfonate, especially mesyloxy or tosyloxy, for example a C_1 - C_3 alkyl halide, especially methyl iodide, or C_1 - C_3 alkyl sulfate, especially dimethyl sulfate, and optionally of formula IV



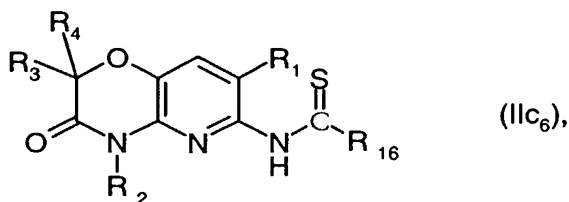
wherein R_2 is as defined for formula I with the exception of R_2 as hydrogen, and L_2 is a leaving group, for example halogen, especially chlorine, bromine or iodine, or sulfonate, especially mesyloxy or tosyloxy, to thereby yield the compound of formula IW₂ wherein R_1 to R_4 , R_{14} , R_{15} and X_3 are as defined and R_{16} is C₁-C₃alkylthio, C₁-C₃haloalkylthio, allylthio or propargylthio (route f) in Reaction Scheme 2,
or, for the preparation of compounds of formula IW₁₉ according to route ka) in Reaction Scheme 2, reacting a compound of formula IIc₄



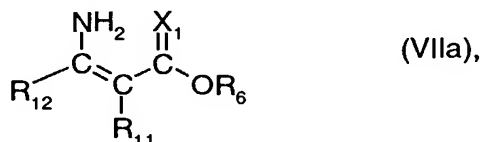
wherein R_1 , R_2 , R_3 and R_4 are as defined hereinbefore, X_0 is oxygen, sulfur or amino, and R_5 is C₁-C₄alkyl or phenyl, with an enamine derivative of formula VIIa



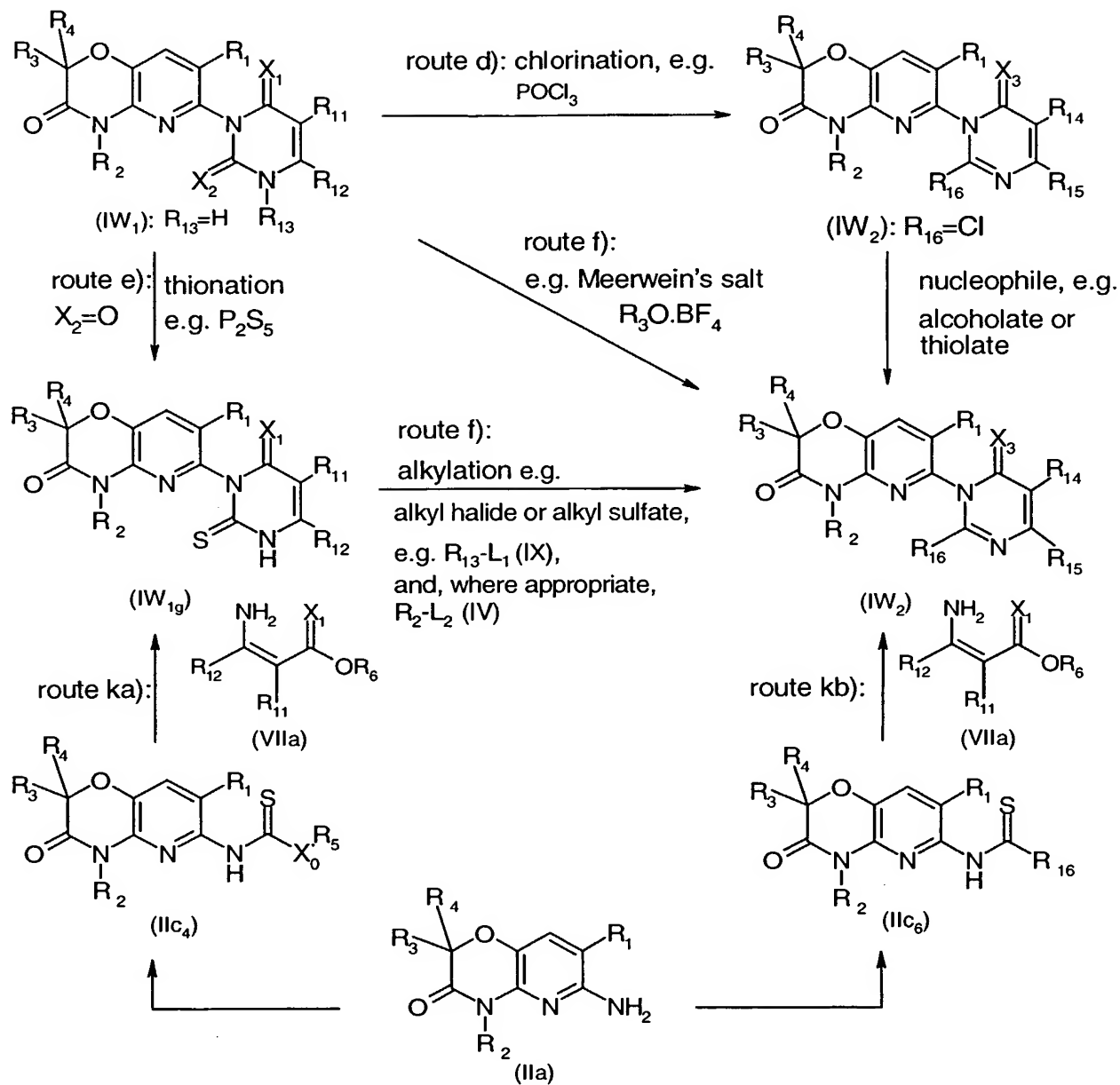
wherein R_{11} , R_{12} and X_1 are as defined and R_6 is C₁-C₄alkyl,
or, according to route kb) in Reaction Scheme 2, reacting a compound of formula IIc₆



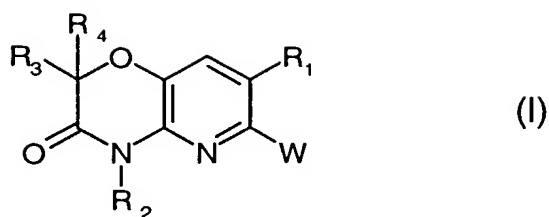
wherein R_1 , R_2 , R_3 and R_4 are as defined and R_{16} is C₁-C₃alkyl or C₁-C₃haloalkyl, with an enamine derivative of formula VIIa



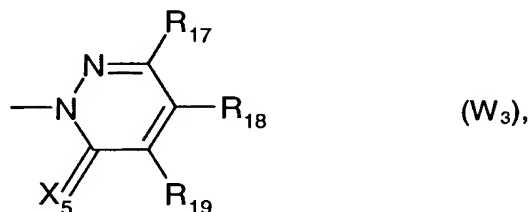
wherein R_{11} , R_{12} and X_1 are as defined and R_6 is C₁-C₄alkyl, to yield the compounds of formula IW₂, wherein R_{14} , R_{15} and X_3 are as defined for R_{11} , R_{12} and X_1 , respectively, in compounds of formulae VIIa and IW₁, and R_{16} is as defined.

Reaction Scheme 2:

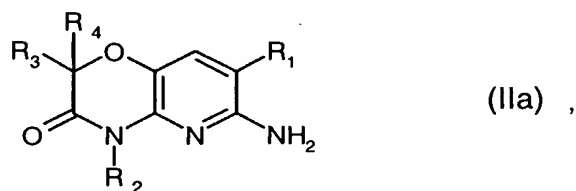
The process according to the invention for the preparation of compounds of formula I according to variant b) and Reaction Scheme 1b) comprises, for the preparation of those compounds of formula I



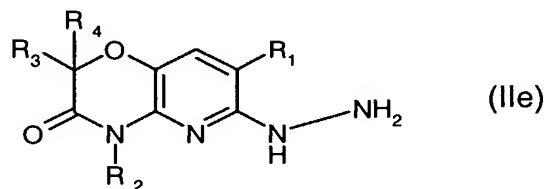
wherein R_1 , R_2 , R_3 and R_4 are as defined for formula I and W is a group W_3



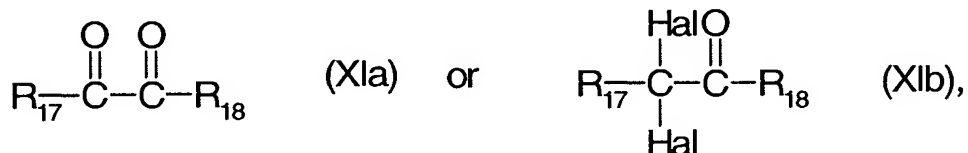
wherein R_{17} , R_{18} , R_{19} and X_5 are as defined for formula I, first of all converting a compound of formula IIa



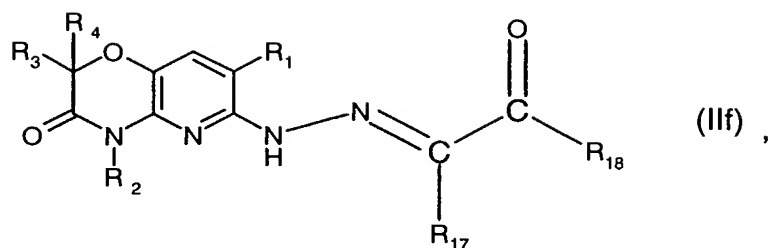
wherein R_1 , R_2 , R_3 and R_4 are as defined for formula I, under standard diazotisation conditions, e.g. using HNO_3/H_2SO_4 , and with reduction of the diazonium salt, as described, for example, in 'Methoden der Organischen Chemie (Houben-Weyl)', volume X/2 (Stickstoffverbindungen), Georg Thieme Verlag, Stuttgart, 1967, pages 180 ff., into the hydrazine derivative of formula IIe



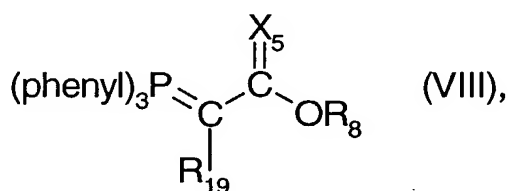
and then condensing that compound with the reagent of formula XIa or XIb



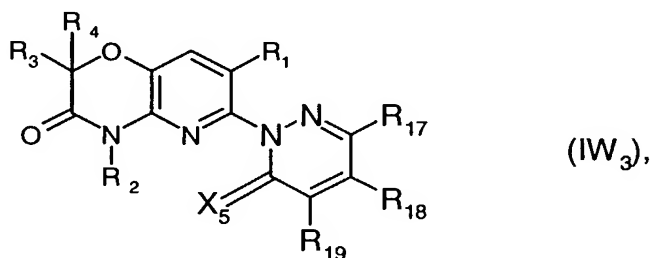
wherein R_{17} and R_{18} are as defined for formula I and Hal is halogen, especially chlorine or bromine, to form the hydrazone derivative of formula IIf



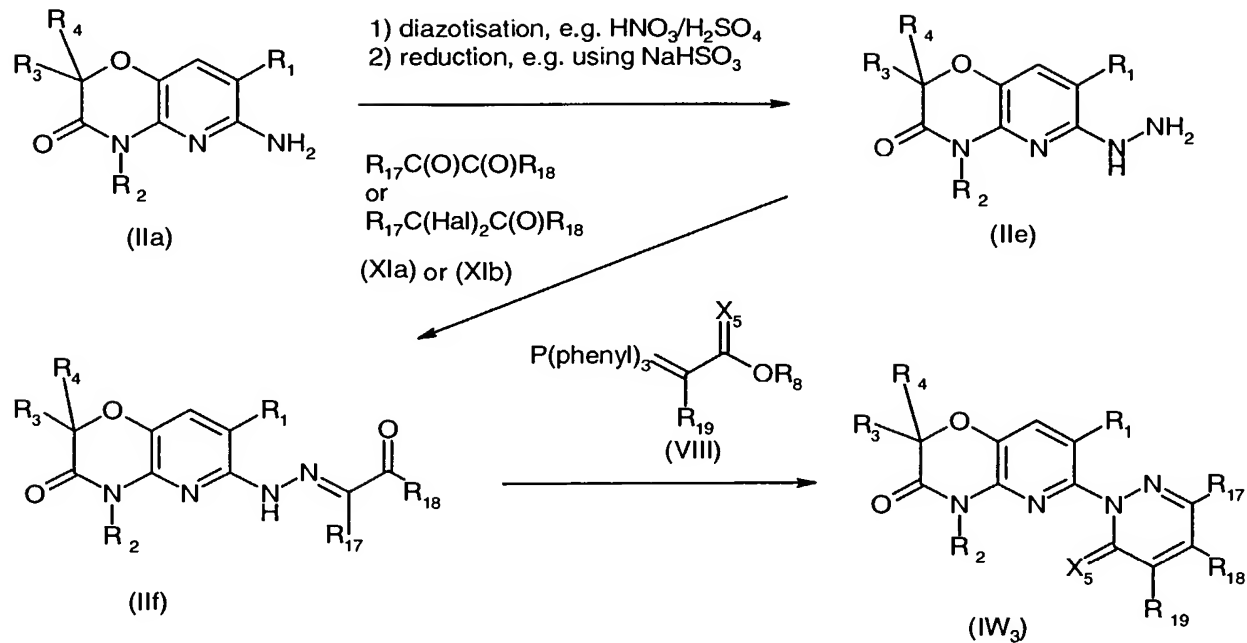
the substituents R_1 , R_2 , R_3 , R_4 , R_{17} and R_{18} in the compounds of formulae IIe and IIIf being defined as indicated, and then condensing and cyclising (as illustrated in Reaction Scheme 3) the compound of formula IIIf with the Wittig reagent of formula VIII



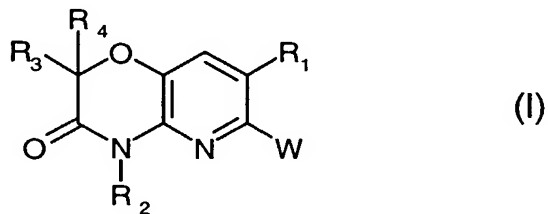
wherein R_{19} and X_5 are as defined for formula I and R_8 is C_1 - C_4 alkyl, in the presence of from 0.01 to 1.5 equivalents of a suitable base, for example an alkali metal hydride or alcoholate, e.g. sodium hydride or potassium tert-butanolate, in an inert solvent, for example an ether, e.g. THF, an aromatic hydrocarbon, e.g. toluene or one of the xylene isomers, or an amide, e.g. NMP, to form the compound of formula IW₃



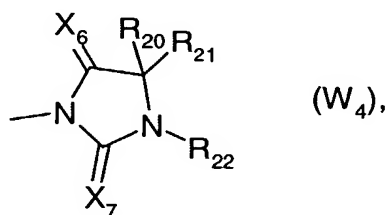
wherein R_1 , R_2 , R_3 , R_4 , R_{17} , R_{18} , R_{19} and X_5 are as defined, and, optionally, further functionalising that compound according to the definitions of R_1 , R_2 , R_{18} and X_5 in analogous manner to that described under aa), ac) or ae).

Reaction Scheme 3:

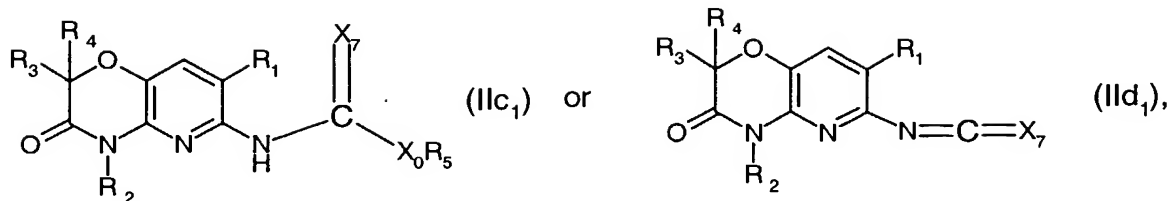
The process according to the invention for the preparation of compounds of formula I according to variant b) and Reaction Scheme 1b is carried out analogously to known processes, as described, for example, in WO 99/52893, EP-A-0 272 594, EP-A-0 493 323, DE-A-3 643 748, WO 95/23509, US-A-5 665 681 and US-A-5 661 109, and comprises, for the preparation of those compounds of formula I



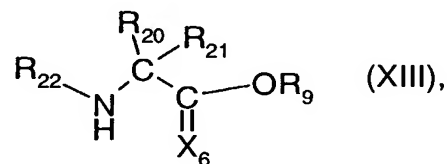
wherein R₁, R₂, R₃ and R₄ are as defined for formula I and W is a group W₄



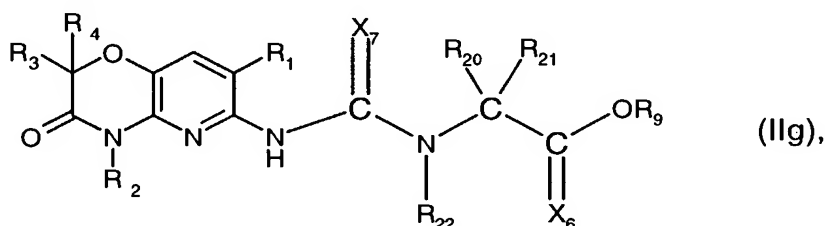
wherein R₂₀, R₂₁, R₂₂ and X₇ are as defined for formula I, reacting a compound of formula IIc₁ or IId₁



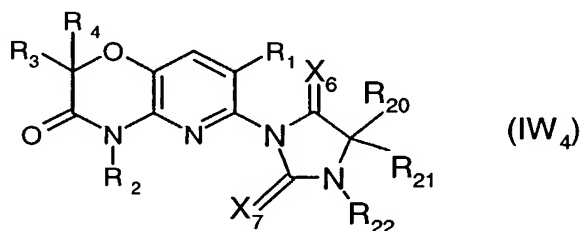
wherein R₁, R₂, R₃, R₄ and X₇ are as defined for formula I, X₀ is oxygen, sulfur or amino, and R₅ is C₁-C₄alkyl, with an amino acid ester of formula XIII



wherein R₂₀, R₂₁, R₂₂ and X₆ are as defined for formula I and R₉ is C₁-C₄alkyl, to form the compound of formula IIg



wherein R₁, R₂, R₃, R₄, R₉, R₂₀, R₂₁, R₂₂, X₆ and X₇ are as defined, and then cyclising (Reaction Scheme 4) the resulting compound to form the compound of formula IW₄



and, optionally, further functionalising that compound according to the definitions of R₁, R₂, R₂₀, R₂₁, R₂₂, X₆ and X₇ in analogous manner to that described under aa), ac) or ae). For example, the compound of formula IW₄ wherein R₂₂ is hydrogen and X₇ is oxygen can, in analogous manner to that described under ac), be further reacted with an alkylating reagent of formula X



wherein R₂₂ is C₁-C₃alkyl and L₅ is a leaving group, for example halogen, especially chlorine, bromine or iodine, or a sulfonate, especially mesyloxy or tosyloxy, in the presence

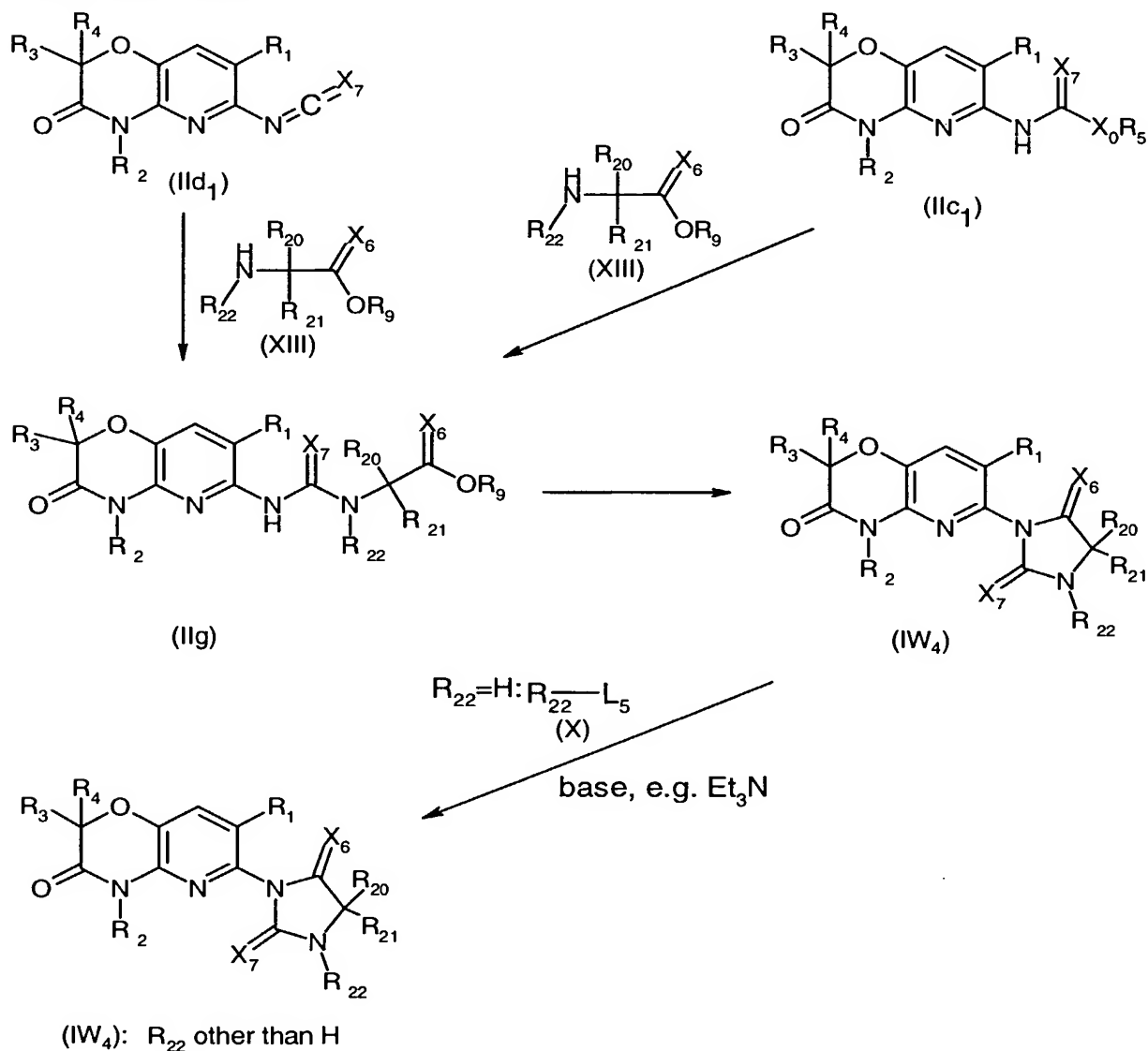
of a suitable base, for example a trialkylamine or an alkali metal carbonate, to form the compound of formula IW₄ wherein R₂₂ is C₁-C₃alkyl.

Moreover, for example, the compound of formula IW₄ wherein R₂₂ and R₂₀ or R₂₂ and R₂₁ together form a C₃-C₅alkylene bridge which is, for example,

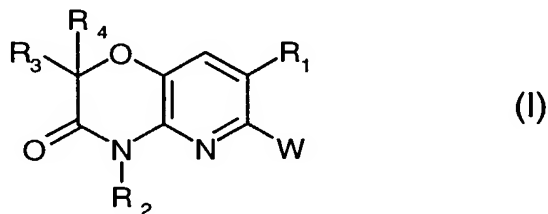
1) interrupted by -C(O)- or substituted by hydroxy, can readily be converted, by standard methods, for example using the reagent DAST (diethylaminosulfur trifluoride) or DeoxyfluorTM (= bis(2-methoxymethyl)aminosulfur trifluoride), into the corresponding derivatives substituted once or twice by fluorine (Example 19), or

2) interrupted by sulfur, can readily be converted, using a suitable oxidising agent, for example sodium periodate (NaIO₄), into the corresponding -S(O)- or -S(O)₂- derivative.

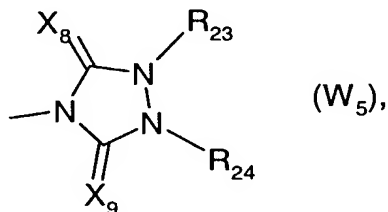
Reaction Scheme 4:



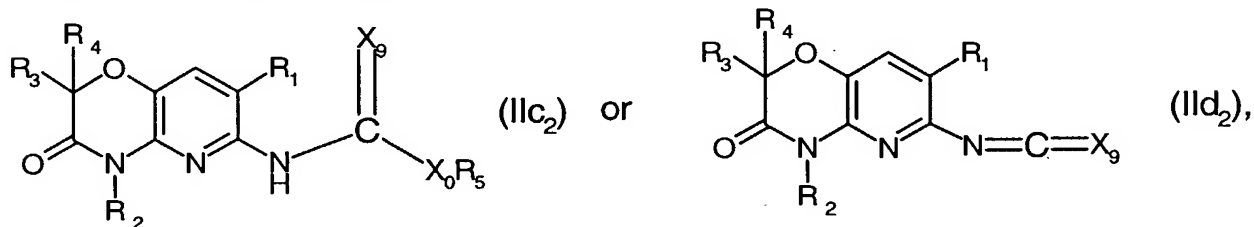
The process according to the invention for the preparation of compounds of formula I according to variant b) and Reaction Scheme 1b is carried out analogously to known processes, as described, for example, in WO 99/52893, EP-A-0 210 137, DE-A-2 526 358, EP-A-0 075 267 and EP-A-0 370 955, and comprises, for the preparation of those compounds of formula I



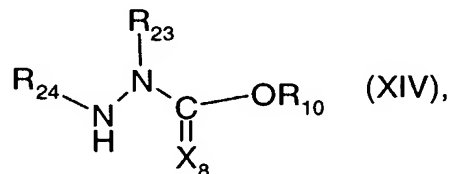
wherein R_1 , R_2 , R_3 and R_4 are as defined for formula I and W is a group W_5



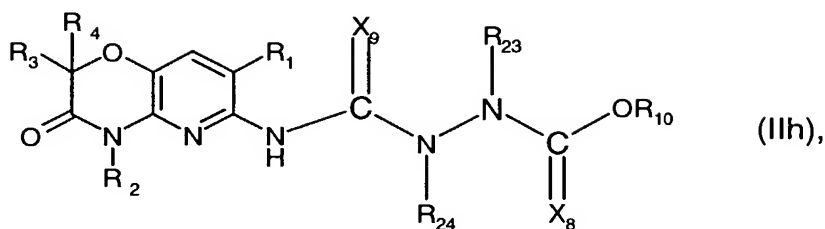
wherein R_{23} , R_{24} , X_8 and X_9 are as defined for formula I, either, according to Reaction Scheme 5, reacting a compound of formula IIc₂ or IIId₂



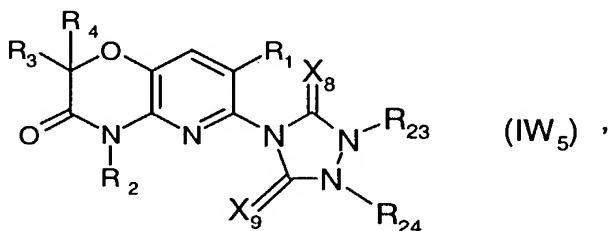
wherein R_1 , R_2 , R_3 , R_4 and X_9 are as defined for formula I, X_0 is oxygen, sulfur or amino, and R_5 is C₁-C₄alkyl, with a hydrazide ester of formula XIV



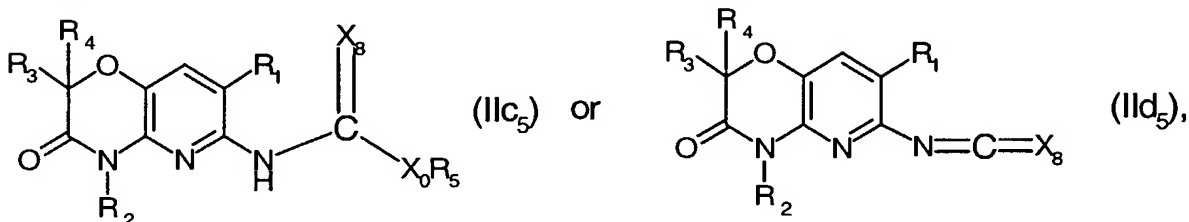
wherein R_{23} , R_{24} and X_8 are as defined for formula I and R_{10} is C₁-C₄alkyl, in the presence of a base, for example a trialkylamine, and a suitable solvent, for example a chlorinated hydrocarbon, e.g. chlorobenzene, or an amide, e.g. DMF or NMP, to thereby yield the compound of formula IIh



wherein R_1 , R_2 , R_3 , R_4 , R_{10} , R_{23} , R_{24} , X_8 and X_9 are as defined, and then cyclising that compound to form the compound of formula IW_5



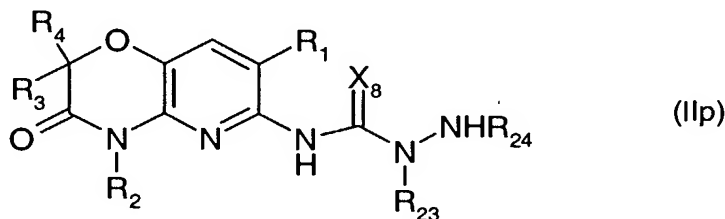
or, according to Reaction Scheme 5a, reacting a compound of formula IIc_5 or IId_5



wherein R_1 , R_2 , R_3 , R_4 , R_5 , X_0 and X_8 are as defined, with a hydrazine of formula XXXVa



wherein R_{23} and R_{24} are as defined, to form the compound of formula IIp

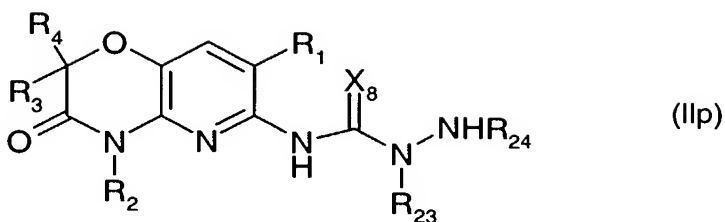


and cyclising that compound, according to route r) in Reaction Scheme 5a, with phosgene, thiophosgene or a chloroformate of formula VIa

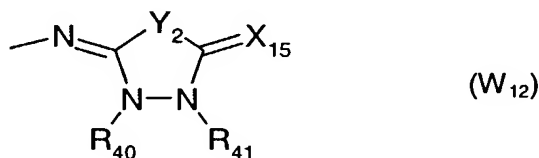


wherein X_9 is as defined and R_9 is C_1 - C_4 alkyl.

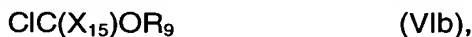
According to Reaction Scheme 5a, route s), starting from the compounds of formula IIp



wherein R_1 , R_2 , R_3 and R_4 are as defined for formula I with the proviso that X_8 , R_{23} and R_{24} are as defined for Y_2 , R_{40} and R_{41} , respectively, the compounds of formula I wherein W is a group W_{12}



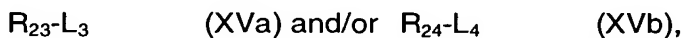
and R_{40} , R_{41} , Y_2 and X_{15} are as defined for formula I, can be obtained by reaction with phosgene, thiophosgene or a chloroformate of formula VIb



wherein X_{15} is as defined and R_9 is $\text{C}_1\text{-C}_4$ alkyl. For example, the compounds of formula IW_{12} can be obtained by reacting compounds of formula IIp with phosgene in an aromatic hydrocarbon, e.g. toluene, and preferably in an additional solvent, for example an ether, e.g. tetrahydrofuran, and in the presence of a base as acid-binding agent, at temperatures of from 5° to 20°C .

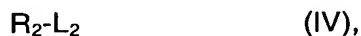
The compound of formula IW_5 may, optionally, be further functionalised according to the definitions of R_1 , R_2 , R_{23} , R_{24} , X_8 and X_9 in analogous manner to that described under aa), ac) or ae).

For example, the compound of formula IW_5 wherein R_{23} and/or R_{24} are hydrogen can be further reacted, in analogous manner to that described under ac), with an alkylating reagent of formula XVa and/or XVb



wherein R_{23} and R_{24} are as defined for formula I with the exception of R_{23} and R_{24} as hydrogen, and L_3 and L_4 are each a leaving group, for example halogen, especially chlorine, bromine or iodine, or a sulfonate, especially mesyloxy or tosyloxy, in the presence of a suitable base to form the compound of formula IW_5 wherein R_{23} and/or R_{24} are $\text{C}_1\text{-C}_3$ alkyl or $\text{C}_1\text{-C}_3$ haloalkyl. Optionally, the compound of formula IW_5 wherein R_2 is hydrogen, and R_{23} and R_{24} are other than hydrogen can be alkylated, in the presence of a base, for example

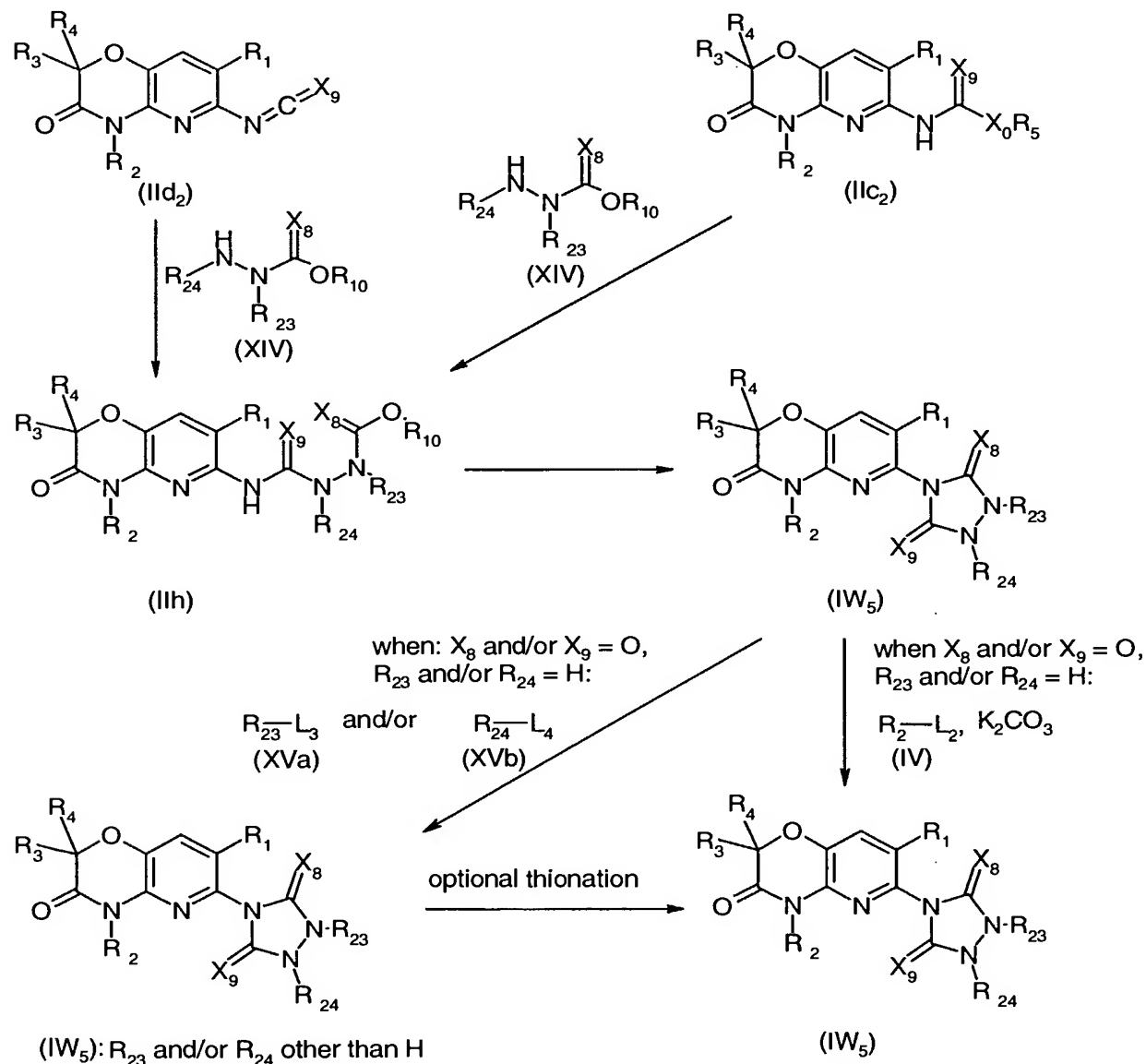
an alkali metal carbonate, e.g. potassium carbonate, as acid-binding agent, with the reagent of formula IV



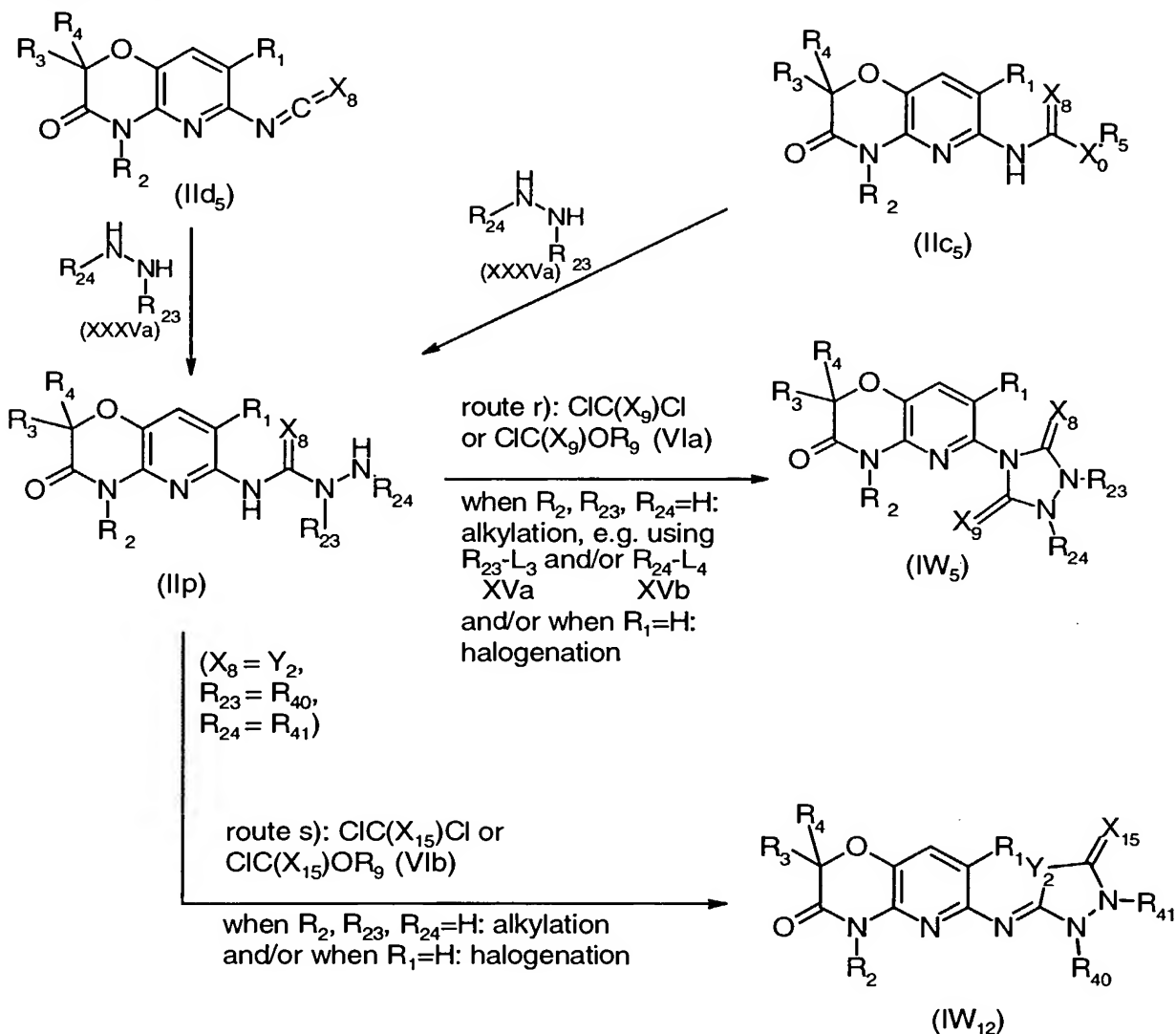
wherein R_2 is as defined for formula I with the exception of R_2 as hydrogen, and L_2 is a leaving group, for example halogen, e.g. chlorine, bromine or iodine, or sulfonate, e.g. mesyloxy or tosyloxy.

Likewise, the compound of formula IW_{12} may be further functionalised (R_1 , R_2 , R_{23} , R_{24} or R_{40} and R_{41} , and X_{15}) in Reaction Scheme 5a according to the standard methods described under aa), ac) and ae). That possibility is also illustrated in Reaction Schemes 5 and 5a.

Reaction Scheme 5:



Reaction Scheme 5a:

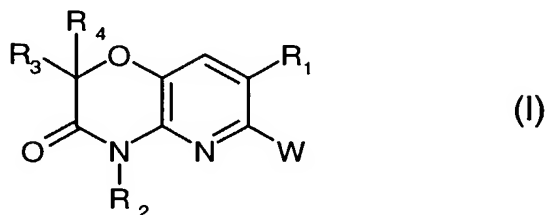


It is also possible to prepare the compounds of formula I wherein W is a group W₆, W₇, W₈, W₉ and W₁₂ analogously to the process according to the invention described above according to variant b) and as illustrated in Reaction Scheme 1b. Such processes are described, for example, in WO 99/52893.

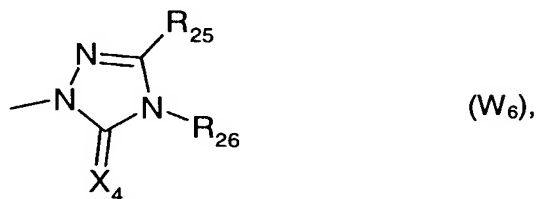
Furthermore, WO 00/15633 describes general processes according to variant b) above, according to which processes it is also possible to prepare the compounds of formula I wherein W is a group W₁, W₂, W₃, W₄, W₅, W₆, W₇, W₈, W₉, W₁₀, W₁₁, W₁₃, W₁₅, W₁₉ or W₂₀.

The process of the invention according to variant b) for the preparation of compounds of formula I is carried out analogously to known processes, as described, for example, in J. Org. Chem. 56, 5643 (1991), J. Heterocycl. Chem. 27, 2017 (1990), DE-OS-3 917 469,

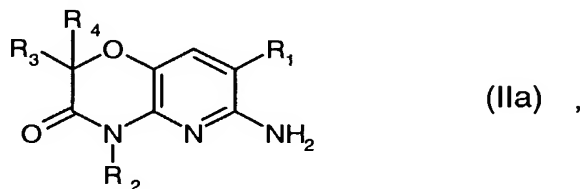
WO 94/22828, WO 88/09617 and US-A-5 449 784, and comprises, for the preparation of those compounds of formula I



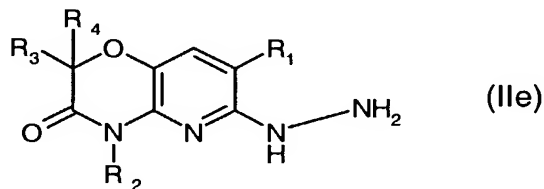
wherein R_1 , R_2 , R_3 and R_4 are as defined for formula I and W is a group W_6



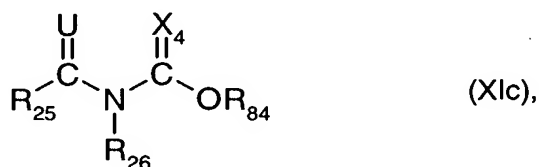
wherein R_{25} , R_{26} and X_4 are as defined for formula I, first of all converting a compound of formula IIa



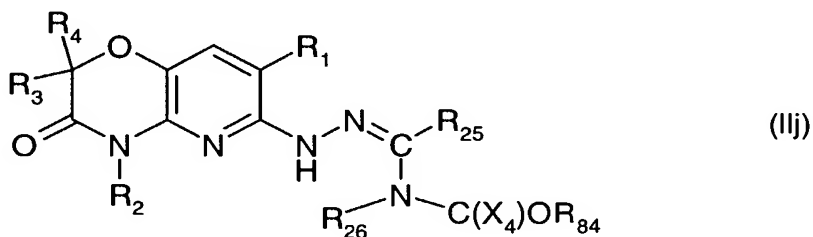
wherein R_1 , R_2 , R_3 and R_4 are as defined for formula I, under diazotisation conditions and with reduction of the diazonium salt, as described, for example, in 'Methoden der Organischen Chemie (Houben-Weyl)', volume X/2 (Stickstoffverbindungen), Georg Thieme Verlag, Stuttgart, 1967, pages 180 ff., into the hydrazine derivative of formula IIe



and then, according to route g) in Reaction Scheme 6, condensing that compound with the reagent of formula XIc



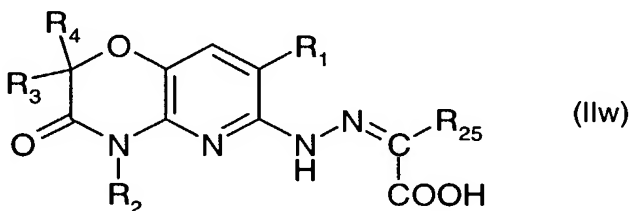
wherein R_{25} , R_{26} and X_4 are as defined, U is oxygen, sulfur or imino, and R_{84} is C_1 - C_4 alkyl, optionally in the presence of a base, for example an alcoholate, e.g. sodium ethanolate or potassium tert-butanolate, or an amine, e.g. triethylamine or pyridine, or a carbonate, e.g. potassium carbonate, in a suitable solvent, for example an alcohol, e.g. ethanol, an amide, e.g. DMF or NMP, or pyridine, at temperatures from 20° to the boiling point of the solvent used, to yield the hydrazone derivative of formula IIj



and then cyclising that compound either with base catalysis, for example using an alcoholate, e.g. sodium ethanolate, or preferably with acid catalysis, for example using a carboxylic acid, e.g. acetic acid, or a sulfonic acid, e.g. p-toluenesulfonic acid, in a suitable solvent as mentioned above or also, for example, in a carboxylic acid, e.g. acetic acid, or, according to route h) in Reaction Scheme 6, condensing the compound of formula IIe with the reagent of formula XId



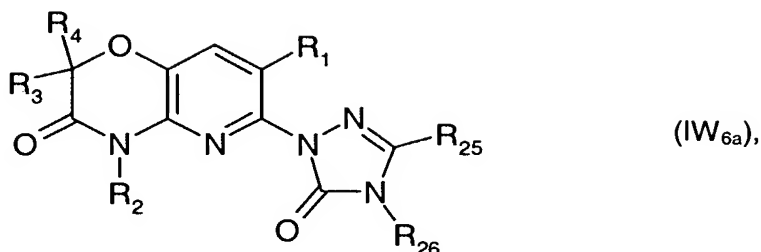
wherein R_{25} is as defined, with acid catalysis, for example using an C_1 - C_4 alkylcarboxylic acid, e.g. propionic acid, a mineral acid, e.g. hydrochloric or sulfuric acid, or a sulfonic acid, e.g. p-toluenesulfonic acid, to yield the hydrazone derivative of formula IIw



and subsequently cyclising that compound in a solvent, for example a halogenated hydrocarbon, e.g. chlorobenzene, or an amide, e.g. NMP, under basic conditions, for example in the presence of an alkali metal hydroxide or alcoholate, e.g. potassium hydroxide or potassium tert-butanolate, with an azide of formula XXXIX



wherein R_{60} is C_1 - C_4 alkyl, to form the compound of formula IW_{6a}



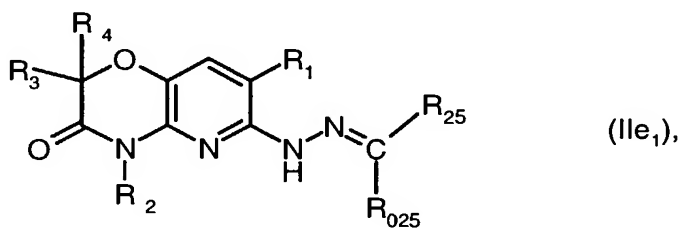
wherein R₁, R₂, R₃, R₄ and R₂₅ are as defined and R₂₆ is hydrogen, and then optionally converting into the compounds of formula IW₆ using the reagent of formula Xa



wherein R₂₆ is C₁-C₄alkyl or C₁-C₄haloalkyl, e.g. methyl or bromodifluoromethyl, and L₅ is a leaving group, for example halogen, especially chlorine, bromine or iodine, or a sulfonate, especially mesyloxy or tosyloxy, in an inert organic solvent, for example a nitrile, e.g. acetonitrile, an amide, e.g. DMF or NMP, a chlorinated hydrocarbon, e.g. chloroform, an aromatic hydrocarbon, e.g. toluene or one of the xylene isomers, or in water, or in a two-phase system consisting of a water-immiscible solvent and water, in the presence of a phase-transfer catalyst, for example a quaternary ammonium salt, e.g. tetrabutylammonium bromide, and in the presence of a base, for example a hydroxide, e.g. an alkali metal hydroxide, or a carbonate, e.g. an alkali metal carbonate, or, according to route i) in Reaction Scheme 6, condensing the compound of formula IIe with a compound of formula XIe



wherein R₂₅ is C₁-C₄alkyl or C₁-C₄haloalkyl, and R₀₂₅ is hydrogen, C₁-C₄alkyl, furyl or phenyl, in a suitable solvent, for example an aromatic hydrocarbon, e.g. one of the xylene isomers, a halogenated hydrocarbon, e.g. chlorobenzene, a ketone, e.g. methyl ethyl ketone, or an amide, e.g. NMP, and optionally with acid catalysis, e.g. using p-toluenesulfonic acid, and at elevated temperatures, advantageously with removal by azeotropic distillation of water of reaction that is formed, to form the hydrazone of formula IIe₁



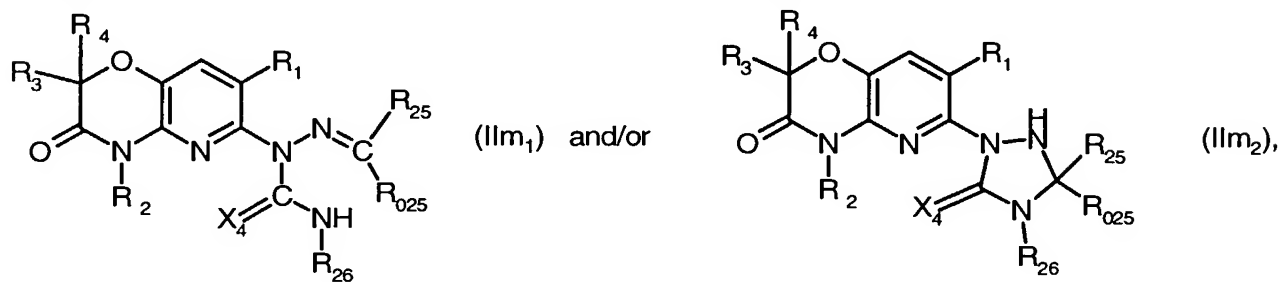
wherein R₁, R₂, R₃, R₄, R₂₅ and R₀₂₅ are as defined, and then reacting that compound with an isocyanate or isothiocyanate of formula XIIf



wherein R_{26} is C_1 - C_4 alkyl or C_1 - C_4 haloalkyl and X_4 is oxygen or sulfur, or with an alkali metal cyanate or alkali metal thiocyanate of formula XIe_1



wherein M^+ is an alkali metal ion and X_4 is as defined (e.g. $Na^+ ^-OCN$, $K^+ ^-OCN$, or $K^+ ^-SCN$), to thereby yield the compound of formula $IIIm_1$ and/or $IIIm_2$

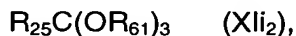


wherein R_1 , R_2 , R_3 , R_4 , R_2 and R_{025} are as defined. This reaction is advantageously carried out in a suitable solvent, for example a ketone, e.g. acetone, an alcohol, e.g. ethanol, a nitrile, e.g. acetonitrile, an amide, e.g. DMF or NMP, or in water, and optionally with addition of a base, for example an amine, e.g. triethylamine, or pyridine, or an acid, e.g. acetic acid or p-toluenesulfonic acid, at temperatures of from 20° to $180^\circ C$.

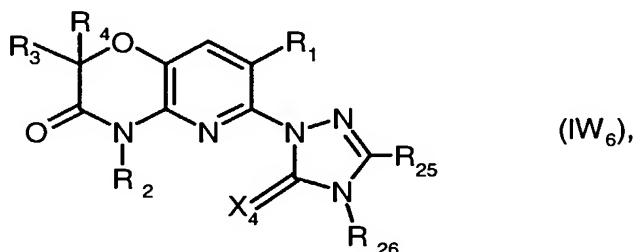
From compounds of formula $IIIm_1$ and/or $IIIm_2$, it is possible, according to route k) in Reaction Scheme 6, either 'in situ' or after their isolation, by reaction with a carboxylic acid of formula XIi or an activated form thereof of formula XIi_1



wherein R_{25} is C_1 - C_4 alkyl or C_1 - C_4 haloalkyl and L_{16} is a leaving group, for example halogen, e.g. chlorine (= acid chloride), or a carboxyl group $-OC(O)R_{25}$ (= anhydride), or with a corresponding ortho ester of formula XIi_2

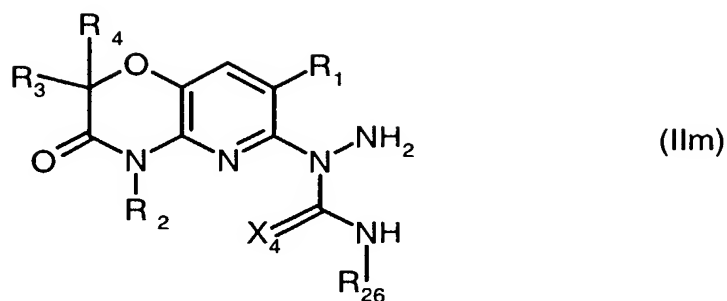


wherein R_{25} is as defined and R_{61} is methyl or ethyl, to yield the compounds of formula IW_6



wherein R_1 , R_2 , R_3 , R_4 , R_{25} , R_{26} and X_4 are as defined.

According to route j) in Reaction Scheme 6, the compounds of formula $IIIm_1$ and/or $IIIm_2$ can first of all be hydrolysed to form the compound of formula $IIIm$



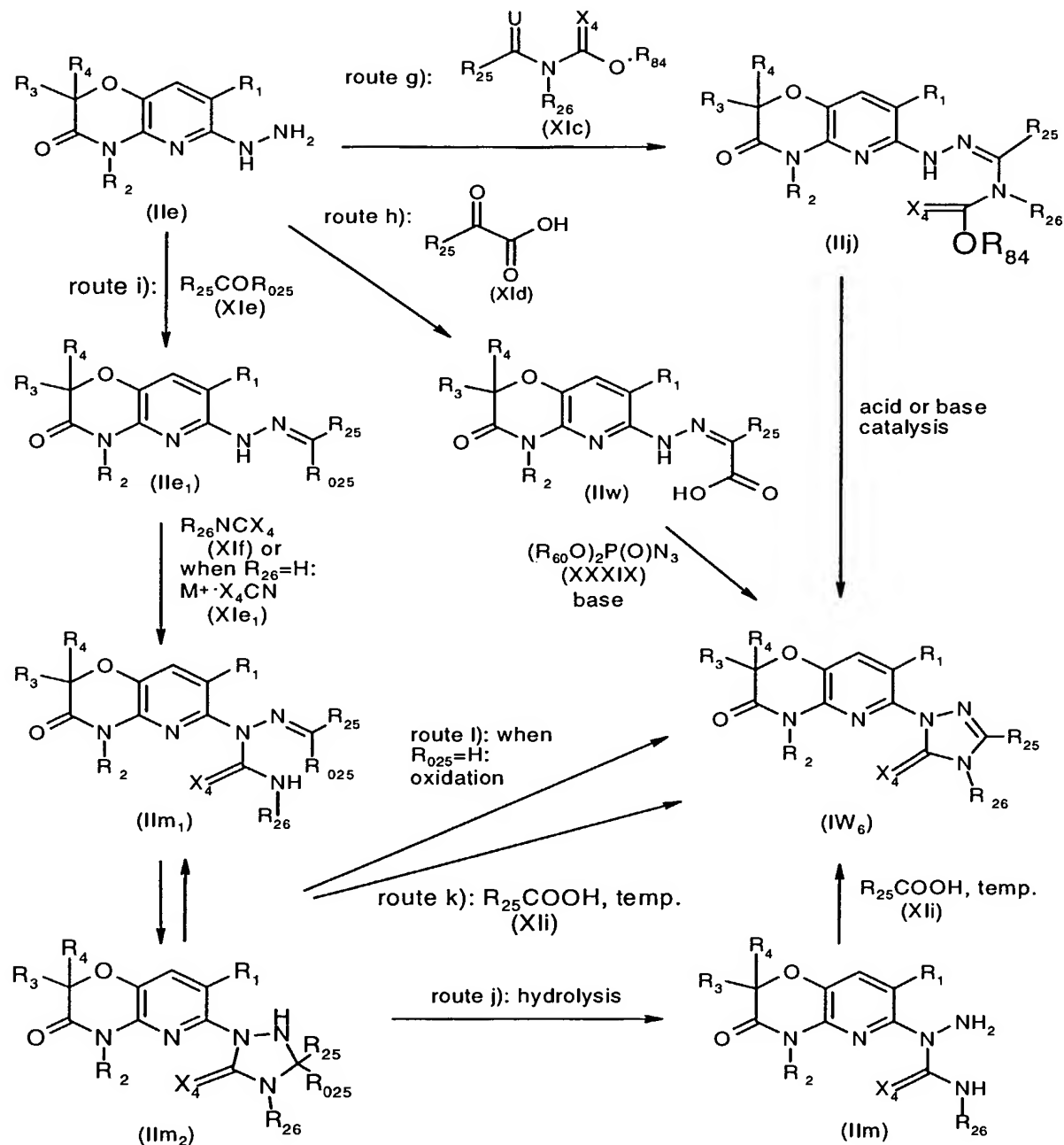
and then, in the presence of a carboxylic acid of formula Xli or an activated form thereof of formula Xli₁ or Xli₂, with heating, cyclised to form the compounds of formula IW₆. The reactions with the carboxylic acid of formula Xli are advantageously carried out without isolation of the compounds of formulae II_{m1} and/or II_{m2} or of formula II_m. The acid of formula Xli can be used in an equimolar amount and also as a solvent, for example acetic or propionic acid.

The compounds of formulae II_{m1} and/or II_{m2} wherein R₀₂₅ is hydrogen can also, according to route I) in Reaction Scheme 6, be converted into the compounds of formula IW₆ in the presence of an oxidising agent, e.g. 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) or Javelle water, in a suitable solvent, for example a halogenated hydrocarbon, e.g. chlorobenzene, a carboxylic acid, e.g. acetic acid, an amide, e.g. NMP, or water, or a mixture thereof, at temperatures of from 0° to 130°C.

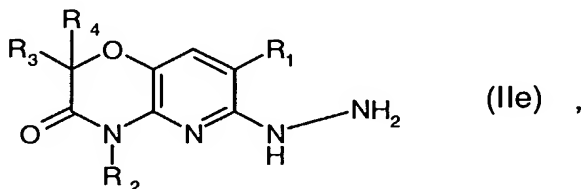
Reaction Scheme 6 illustrates those reactions, which are especially suitable for the preparation of compounds of formula IW₆ wherein R₂₅ is hydrogen, C₁-C₄alkyl or C₁-C₄haloalkyl or wherein R₂₆ and R₂₅ together form a C₃-C₅alkylene bridge.

The compounds of formulae IW_{6a} and IW₆ wherein R₂₆ and/or R₂ are hydrogen or R₁ is hydrogen and X₄ is oxygen may optionally be further functionalised, according to the definitions of R₁, R₂, R₂₆ and X₄, as described above under ab) or ac) using an alkylating reagent, for example R₂₆-L₁ and R₂-L₂, or as described above under ae) or aa).

Reaction Scheme 6:



Starting from the compound of formula Ile



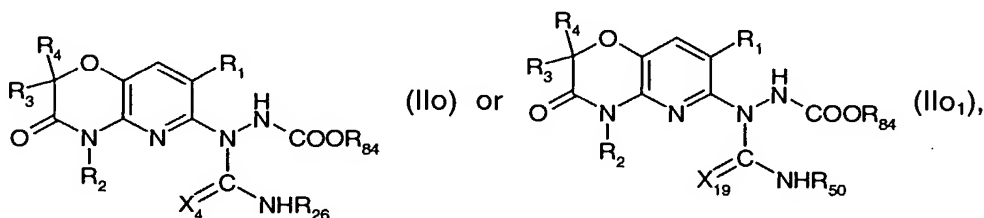
wherein R_1 , R_2 , R_3 and R_4 are as defined for formula I, it is also possible to prepare (according to variant b) and Reaction Scheme 1b) the compounds of formula I wherein W is a group W_6 (compounds of formula IW_6), W_{16} (compounds of formula IW_{16}) or W_{17} (compounds of formula IW_{17}) by reacting the compound of formula IIe first with a chloroformic acid ester of formula XXXIVa



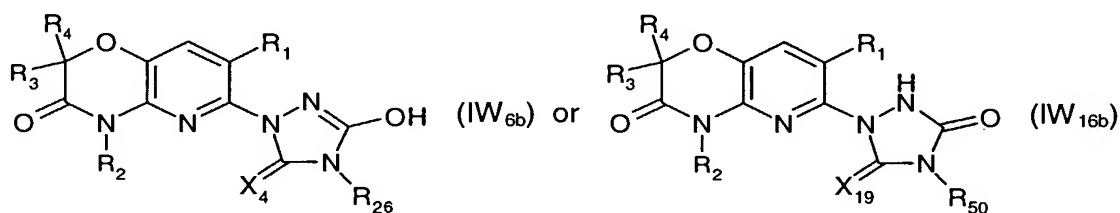
wherein R_{84} is C_1 - C_4 alkyl, and then with an isocyanate or isothiocyanate of formula XI f or XI g



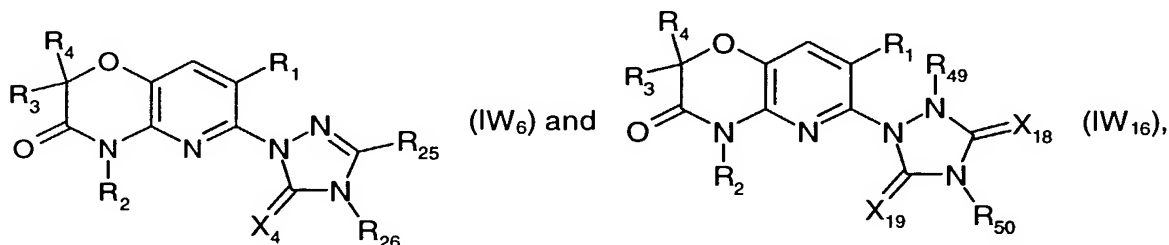
wherein R_{26} and R_{50} are C_1 - C_4 alkyl or C_1 - C_4 haloalkyl and X_4 and X_{19} are oxygen or sulfur, to yield the compound of formula IIo or IIo₁, respectively,



wherein R_1 , R_2 , R_3 , R_4 , R_{26} , R_{50} , R_{84} , X_4 and X_{19} are as defined, and then, under acid conditions, for example in the presence of acetic acid or propionic acid, and optionally at an elevated temperature of up to 130°C , converting that compound into the compound of formula IW_{6b} or IW_{16b}



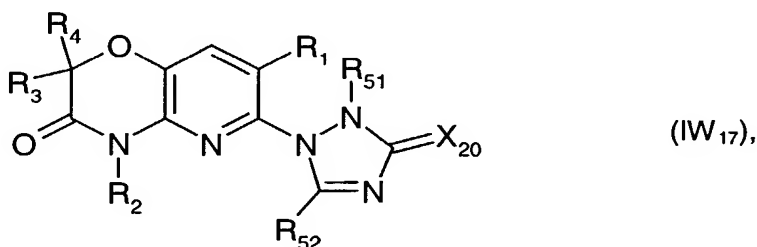
and, using standard processes, carrying out either alkylation (R_2 , R_{25} and R_{26} or R_2 , R_{49} and R_{50} = alkyl) according to ab) or ac) and/or thionation (X_4 , X_{18} and/or X_{19} = S) and optionally alkylation (R_{25}) according to aa) and/or optionally halogenation (R_1 , R_{25} = halogen) according to ae), to yield the compounds of formulae IW_6 and IW_{16}



wherein R_3 , R_4 , X_4 , X_{18} and X_{19} are as defined, R_1 is hydrogen or halogen, R_{25} is halogen, C_1 - C_4 alkoxy or C_1 - C_4 alkylthio and R_2 , R_{26} , R_{49} and R_{50} are each independently of the others hydrogen or alkyl. For example, the compound of formula IW_6 wherein R_{26} is other than hydrogen and X_4 is sulfur can be alkylated with the reagent of formula IV



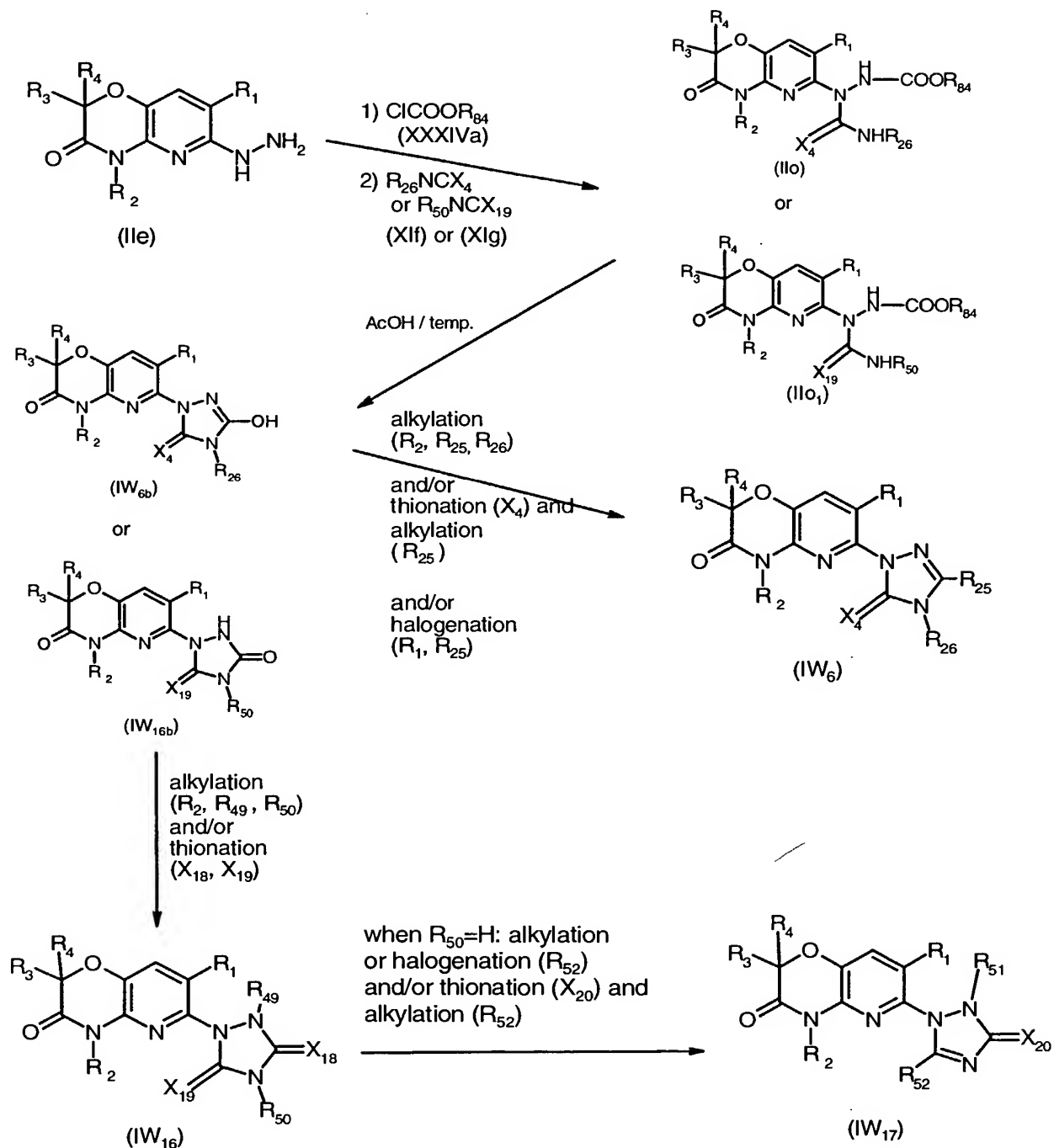
wherein R_2 is as defined for formula I with the exception of R_2 as hydrogen, and L_2 is a leaving group, for example halogen, especially chlorine, bromine or iodine, in the presence of an alkali metal carbonate. When R_{50} in the compound of formula IW_{16} is hydrogen, that compound can, according to standard processes, be subsequently alkylated ($R_{52} = C_1$ - C_3 alkoxy, C_1 - C_3 alkylthio), thionated ($X_{20} = \text{sulfur}$) and/or halogenated (R_1 , $R_{52} = \text{halogen}$) to yield the compound of formula IW_{17}



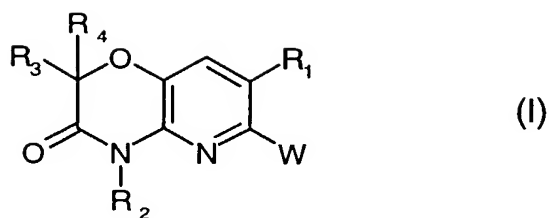
wherein R_1 , R_2 , R_3 and R_4 are as defined, X_{20} is oxygen or sulfur, R_{51} is C_1 - C_4 alkyl and R_{52} is halogen, C_1 - C_3 alkoxy or C_1 - C_3 alkylthio. Reaction Scheme 6a illustrates those reactions.

The above reaction sequence is especially suitable for preparing compounds of formula IW_6 wherein R_{25} is hydroxy, halogen, C_1 - C_4 alkoxy, C_1 - C_4 haloalkoxy, C_1 - C_4 alkylthio, C_1 - C_4 haloalkylthio, C_1 - C_4 alkylsulfinyl, C_1 - C_4 haloalkylsulfinyl, C_1 - C_4 alkylsulfonyl, C_1 - C_4 haloalkylsulfonyl or cyano and also for compounds of formulae IW_{16} and IW_{17} wherein R_{49} , R_{50} , R_{51} , R_{52} , X_{18} , X_{19} and X_{20} are as defined above.

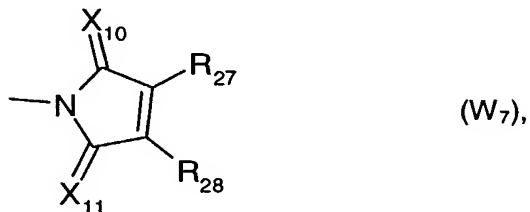
Reaction Scheme 6a:



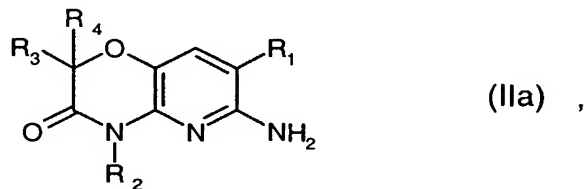
The process according to the invention for the preparation of compounds of formula I is carried out analogously to known processes, as described, for example, in DE-OS-3 917 469 and WO 00/15633, and comprises, for the preparation of those compounds of formula I



wherein R_1 , R_2 , R_3 and R_4 are as defined for formula I and W is a group W_7



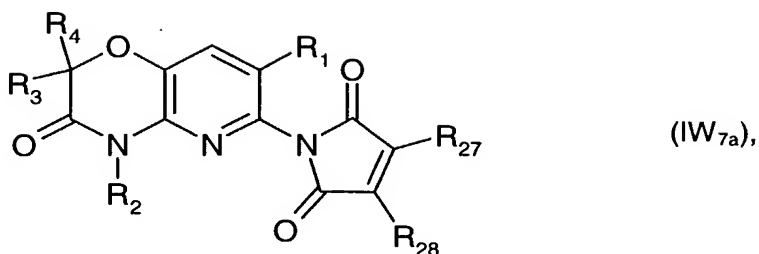
wherein R_{27} , R_{28} , X_{10} and X_{11} are as defined for formula I, reacting a compound of formula IIa



wherein R_1 , R_2 , R_3 and R_4 are as defined for formula I, in the presence of a C_1 - C_4 alkylcarboxylic acid, for example acetic acid or propionic acid, optionally in an inert solvent, for example a halogenated hydrocarbon, e.g. chlorobenzene, with a compound of formula XXXIII

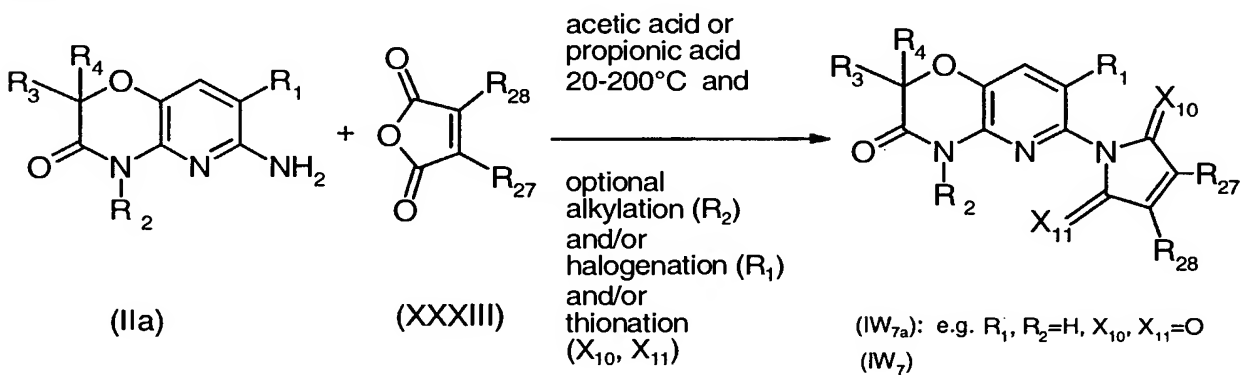


wherein R_{27} and R_{28} are as defined for formula I, in a temperature range of from 20° to 200°C. Reaction Scheme 7 and Example P15 illustrate that reaction sequence. The resulting compound of formula IW_{7a}

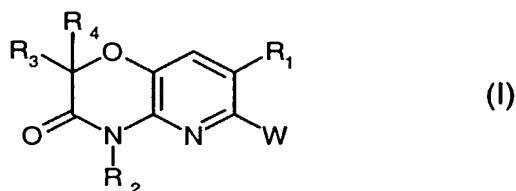


wherein, for example, R₁ and/or R₂ are hydrogen, may be further functionalised according to the definitions of R₁, R₂, X₁₀ and X₁₁ in accordance with processes described under aa), ac) and ae) to form compounds of formula IW₇.

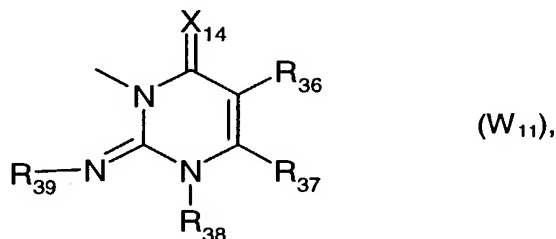
Reaction Scheme 7:



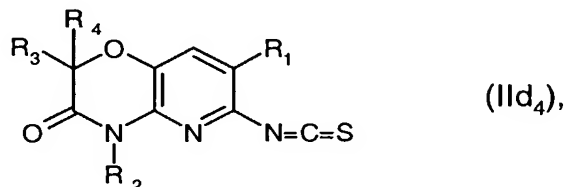
The process according to the invention for the preparation of compounds of formula I is carried out analogously to known processes, as described, for example, in WO 00/15633, and comprises, for the preparation of those compounds of formula I



wherein R₁, R₂, R₃ and R₄ are as defined for formula I and W is a group W₁₁



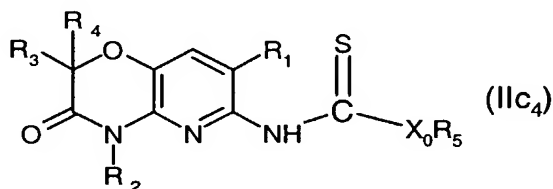
wherein R_{36} , R_{37} , R_{38} and R_{39} are as defined for formula I and X_{14} is oxygen (compound of formula IW_{11a} in Reaction Scheme 17), either, according to route o) in Reaction Scheme 17, reacting a compound of formula II_{d4}



wherein R_1 , R_2 , R_3 and R_4 are as defined, with a compound of formula XXXVIII



wherein R_5 is C₁-C₄alkyl and X_0 is oxygen, sulfur or amino, to yield the compound of formula II_{c4}



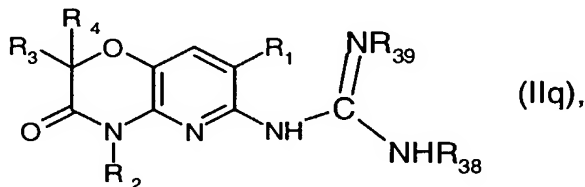
and further reacting that compound in succession with the amines of formulae XXXVIIIa and XXXVIIIb



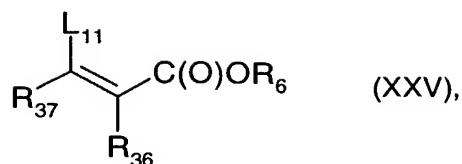
or with the diamine derivative of formula XXXVIIIc



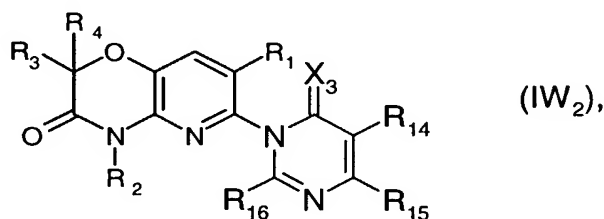
wherein in the compounds of formulae XXXVIIIa and XXXVIIIb R_{38} is C₁-C₃alkyl and R_{39} is hydrogen or C₁-C₃alkyl and in the compound of formula XXXVIIIc R_{38} and R_{39} together form a C₂- or C₃-alkylene bridge, to form the open-chain or cyclic amine derivative of formula II_q



wherein R_1 , R_2 , R_3 , R_4 , R_{38} and R_{39} are as defined, and then condensing that compound with a compound of formula XXV



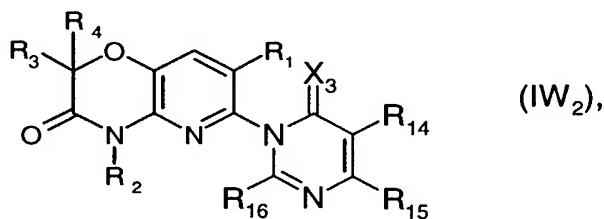
wherein R_{36} and R_{37} are as defined, R_6 is C_1 - C_4 alkyl and L_{11} is hydroxy, C_1 - C_3 alkoxy, chlorine, amino or C_1 - C_3 alkylamino, or, according to route p) in Reaction Scheme 17, first of all reacting a compound of formula IW_2



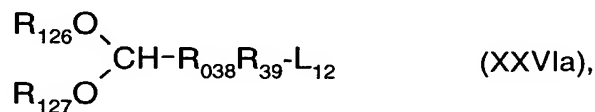
wherein R_1 , R_2 , R_3 , R_4 , X_3 , R_{14} and R_{15} are as defined for formula I and R_{16} is C_1 - C_3 alkylthio, with an oxidising agent, for example hydrogen peroxide, to form the corresponding C_1 - C_3 alkylsulfonyl derivative of formula IW_2 wherein R_{16} is C_1 - C_3 alkylsulfonyl, and converting that derivative, by means of aminolysis, for example using gaseous ammonia in ethanol, or using aqueous ammonium hydroxide, or using an amine of formula XXXVIII d or XXXVIII d_1



wherein R_{016} is hydrogen, C_1 - C_3 alkyl, allyl or propargyl, into the compound of formula IW_2



wherein R_1 , R_2 , R_3 , R_4 , X_3 , R_{14} and R_{15} are as defined and R_{16} is amino, C_1 - C_3 alkylamino, di(C_1 - C_3 alkyl)amino, allylamino, diallylamino, propargylamino or dipropargylamino, and then reacting that compound, when R_{16} is amino, with an aldehyde derivative of formula XXVI a



wherein R_{126} is C_1 - or C_2 -alkyl and R_{127} is hydrogen or C_1 - or C_2 -alkyl, R_{038} and R_{39} together form a C_1 - or C_2 -alkylene bridge and L_{12} is a leaving group, for example chlorine, bromine, iodine, mesyloxy or tosyloxy, or with the reagent of formula XXVI b



wherein R_{38} and R_{39} together form a C_2 - or C_3 -alkylene bridge, L_{12} and L_{13} are each a leaving group, for example chlorine, bromine, iodine, mesyloxy or tosyloxy, or with the alkylating agent of formula XXVIa



wherein R_{38} is C_1 - C_3 alkyl and L_{12} is a leaving group, for example chlorine, bromine or iodine, or a sulfonate, especially mesyloxy or tosyloxy, or, according to route q) in Reaction Scheme 17, first of all reacting the compound of formula IW_2 with an oxidising agent, for example hydrogen peroxide, and then with a reagent of formula XXVIc



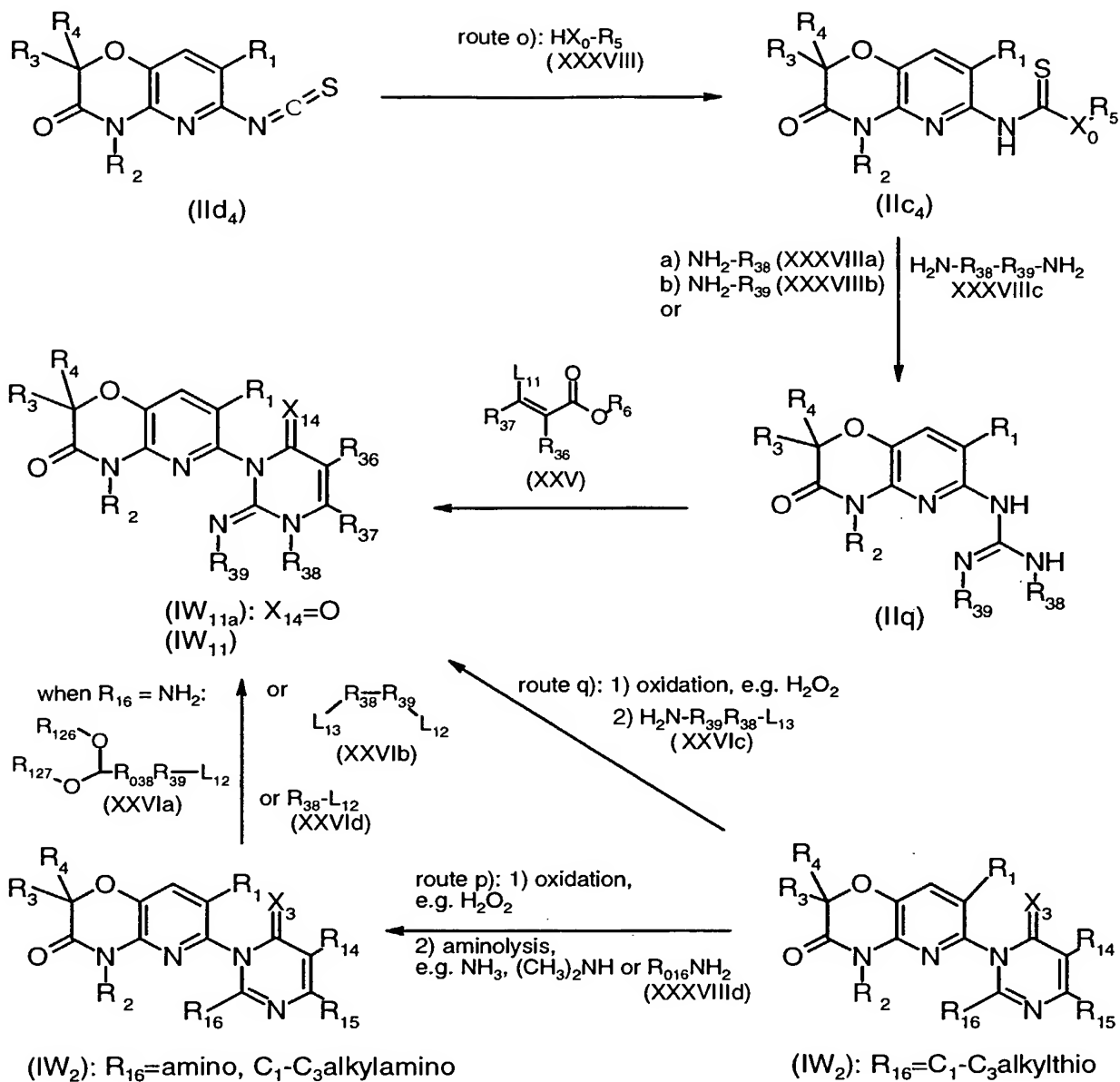
wherein R_{38} and R_{39} together form a C_2 - or C_3 -alkylene bridge and L_{13} is as defined, wherein according to routes p) and q) in Reaction Scheme 17 the substituents X_{14} , R_{36} and R_{37} in compounds of formulae IW_{11} and IW_{11a} take the meanings of the corresponding substituents X_3 , R_{14} and R_{15} , respectively, in the starting compound IW_2 , and R_{38} and R_{39} together form a C_2 - or C_3 -alkylene or -alkenylene bridge.

The resulting compounds of formulae IW_{11} and IW_2 wherein R_1 , R_2 , R_3 , R_4 , R_{14} , R_{15} , R_{36} , R_{37} , R_{38} , R_{39} , X_3 and X_{14} are as defined and R_{16} is C_1 - C_3 alkylsulfinyl, C_1 - C_3 alkylsulfonyl, amino, C_1 - C_3 alkylamino, di(C_1 - C_3 alkyl)amino, allylamino or propargylamino, may be further functionalised in accordance with the standard methods described above: when X_{14} or X_3 is oxygen, in accordance with aa) using a thionating reagent; when R_{38} is hydrogen, in accordance with ab) using an alkylating reagent of formula IXa

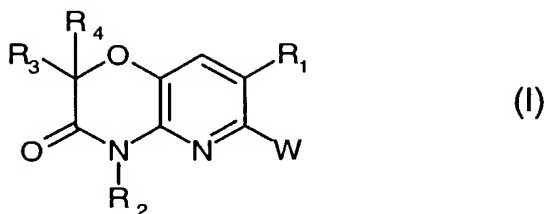


wherein R_{38} is as defined for formula I and L_1 is a leaving group, for example halogen, especially chlorine, bromine or iodine, or a sulfonate, especially mesyloxy or tosyloxy; when R_2 is hydrogen, in accordance with ac) using an alkylating reagent of formula IV; and, when R_1 and/or R_{36} are hydrogen, in accordance with ae) using a halogenating reagent.

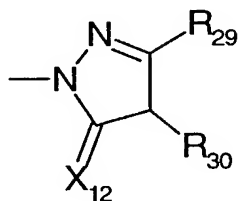
Reaction Scheme 17:



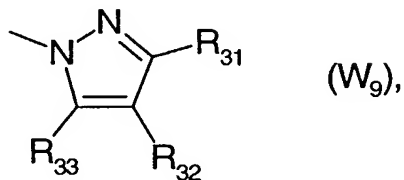
The process according to the invention for the preparation of compounds of formula I is carried out analogously to known processes, as described, for example, in DE-OS-3 917 469, WO 00/15633 and US-A-4 831 150, and comprises, for the preparation of those compounds of formula I



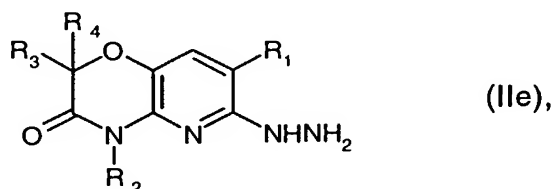
wherein R_1 , R_2 , R_3 and R_4 are as defined for formula I and W is a group W_8 or W_9



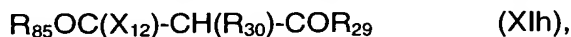
or



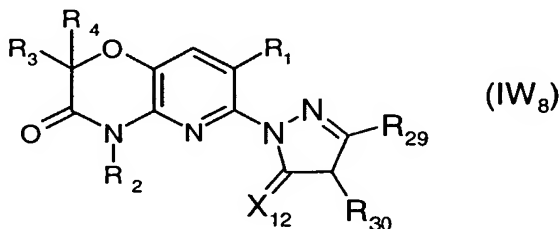
wherein R_{29} , R_{30} , R_{31} , R_{32} , R_{33} and X_{12} are as defined for formula I, condensing with one another a compound of formula IIe



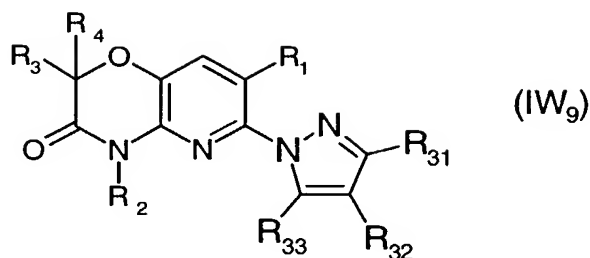
wherein R_1 , R_2 , R_3 and R_4 are as defined, and a compound of formula XIh



wherein R_{29} , R_{30} and X_{12} are as defined and R_{85} is C_1 - C_4 alkyl or phenyl, optionally in an organic acid, for example acetic acid or propionic acid, and a further inert solvent, for example a halogenated hydrocarbon, e.g. chlorobenzene, by heating at from 20° to 200°C to yield the compound of formula IW₈

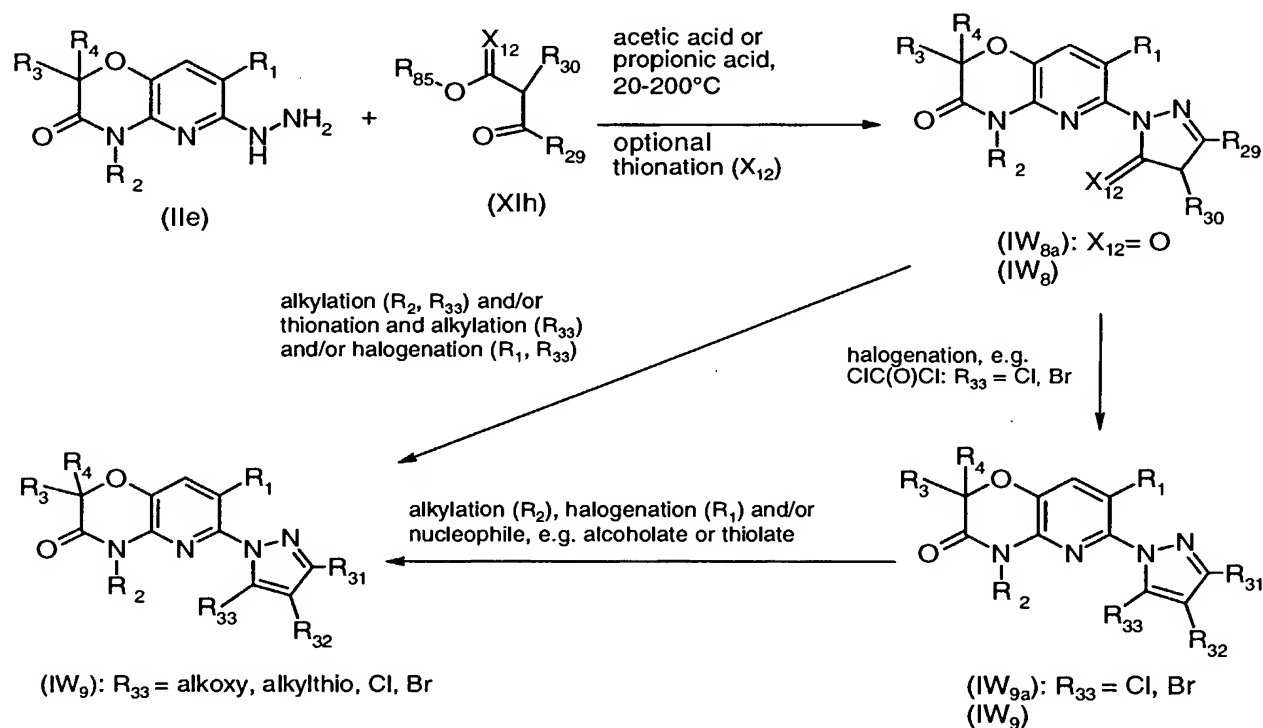


That compound may be further functionalised in accordance with the standard methods aa), ac) and/or ae) described above. In particular, it is possible, starting from the compound of formula IW₈, to obtain, by means of halogenation, for example using phosgene, oxalyl chloride, thionyl chloride, phosphorus oxychloride or phosphorus pentachloride, phosphorus oxybromide or phosphorus tribromide (R_1 , R_{33}), and/or alkylation (R_2 , R_{33}) and/or thionation and alkylation (R_{33}), the compound of formula IW₉

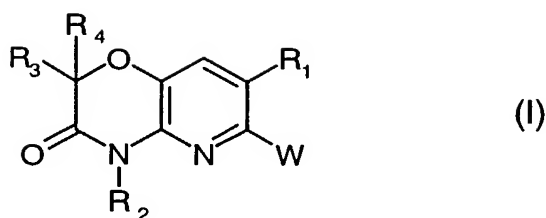


wherein R₁, R₂, R₃ and R₄ are as defined, R₃₁ and R₃₂ have the meanings of R₂₉ and R₃₀, respectively, in the compound of formula IW₈ and R₃₃ is halogen, hydroxy, C₁-C₃alkoxy, C₁-C₃haloalkoxy, mercapto, C₁-C₃alkylthio, C₁-C₃alkylsulfinyl or C₁-C₃alkylsulfonyl. Reaction Scheme 10 illustrates those reaction steps.

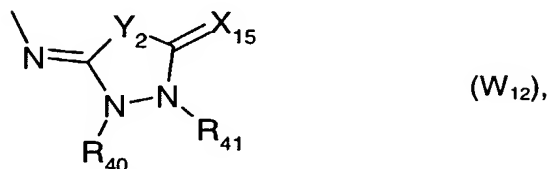
Reaction Scheme 10:



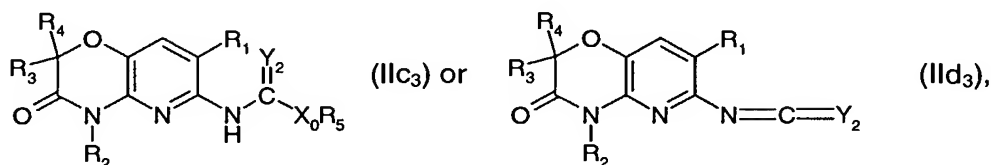
The process according to the invention for the preparation of compounds of formula I is carried out analogously to known processes and comprises, for the preparation of those compounds of formula I



wherein R_1 , R_2 , R_3 and R_4 are as defined for formula I and W is a group W_{12}



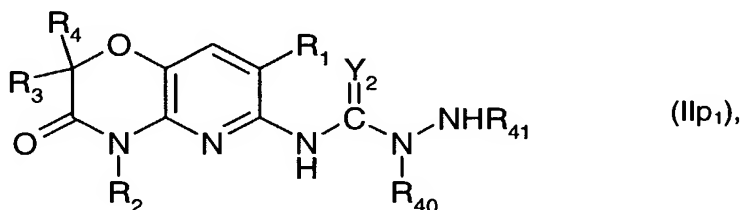
wherein R_{40} , R_{41} , X_{15} and Y_2 are as defined for formula I, reacting a compound of formula IId₃ or IIc₃



wherein R_1 , R_2 , R_3 , R_4 and Y_2 are as defined for formula I, R_5 is C_1 - C_4 alkyl and X_0 is oxygen, sulfur or amino, with a compound of formula XXXV



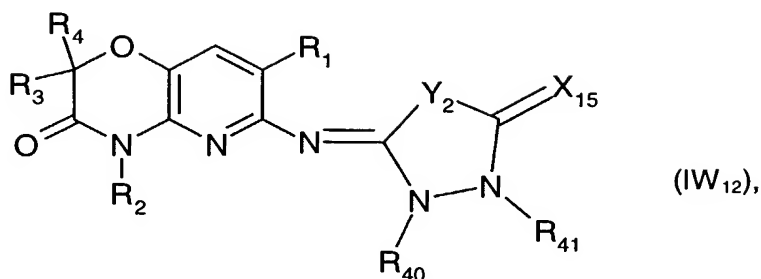
wherein R_{40} and R_{41} are as defined for formula I, to yield the compound of formula IIp₁



and further reacting that compound with the compound of formula XXXVI



wherein X_{15} is oxygen or sulfur, and L_6 and L_7 are leaving groups, for example halogen, e.g. chlorine or bromine (phosgene, thiophosgene), or L_7 may additionally be hydroxy or C_1 - C_4 alkoxy (haloformic acid or an ester thereof). That (thio)phosgenation reaction is carried out at temperatures of from 0° to 80°C , preferably from 5° to 25°C . Reaction Scheme 8 illustrates that reaction sequence. The resulting compounds of formula IW₁₂



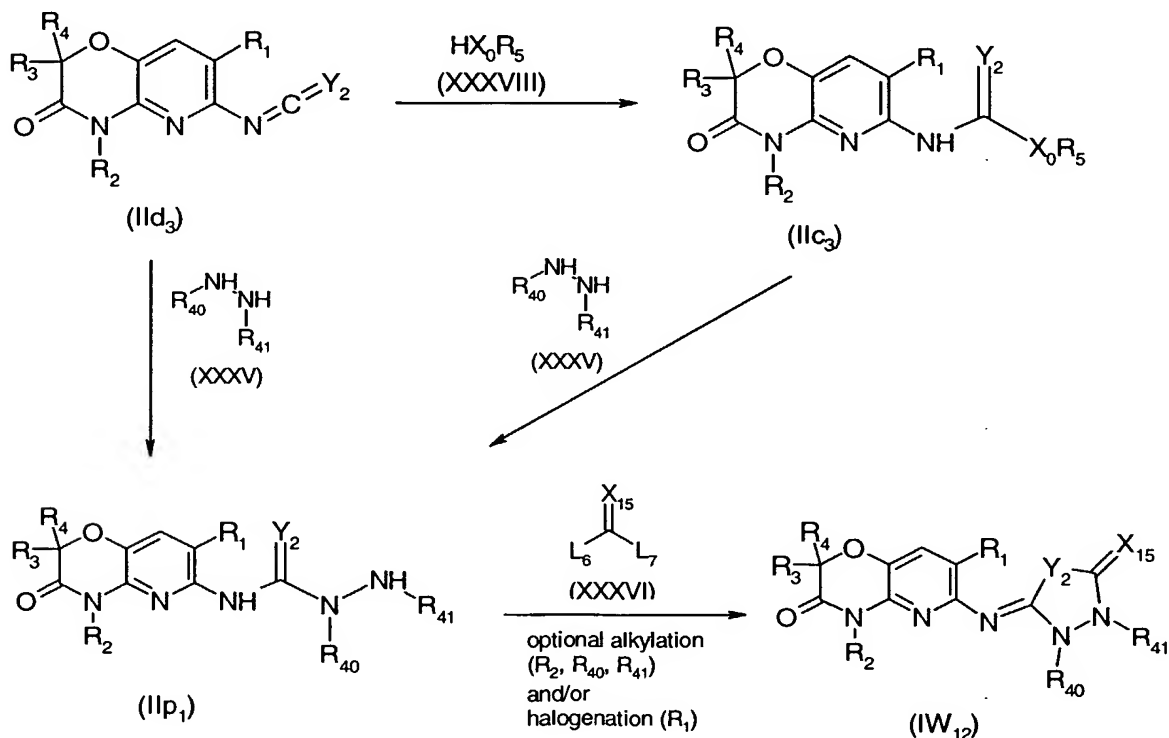
wherein, for example, R₁, R₂, R₄₀ and R₄₁ are hydrogen and X₁₅ is oxygen, may be further functionalised according to the definitions of R₁, R₂, R₄₀, R₄₁ and X₁₅ in accordance with processes described under aa), ac), ad) and ae).

The iso-(thio-)cyanate derivative of formula IIc₃ may, in addition, be converted into the compound of formula IIc₃ by reaction with a reagent of formula XXXVIII



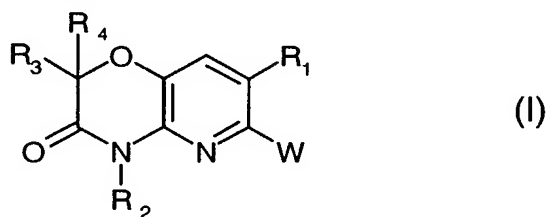
wherein R₅ is C₁-C₄alkyl and X₀ is oxygen, sulfur or amino.

Reaction Scheme 8:

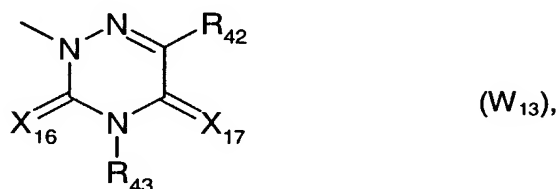


The process according to the invention for the preparation of compounds of formula I is carried out analogously to known processes, as described, for example, in Helv. Chim. Acta

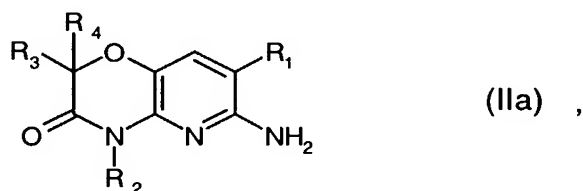
61, 1175 (1978), J. Heterocycl. Chem. 17, 1365 (1980) and WO 97/30980, and comprises, for the preparation of those compounds of formula I



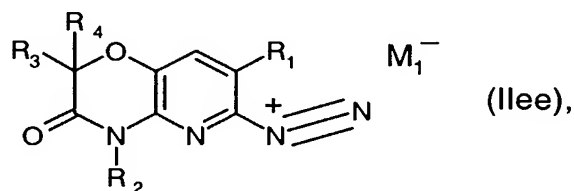
wherein R₁, R₂, R₃ and R₄ are as defined for formula I and W is a group W₁₃



wherein R₄₂, R₄₃, X₁₆ and X₁₇ are as defined for formula I, first of all converting a compound of formula IIa



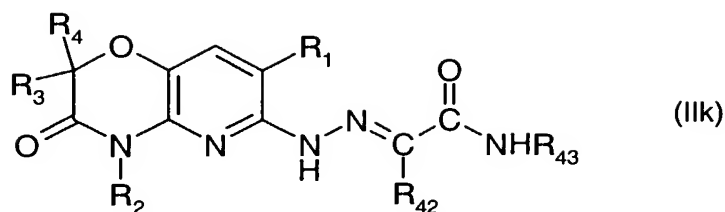
wherein R₁, R₂, R₃ and R₄ are as defined for formula I, under diazotisation conditions, into the diazonium salt of formula IIee



wherein R₁, R₂, R₃ and R₄ are as defined and M₁⁻ is an anion, for example hydrogen sulfate or tetrafluoroborate, or halide, for example chloride, and then, in accordance with route m) in Reaction Scheme 9, coupling that salt with the reagent of formula XXXVIIa



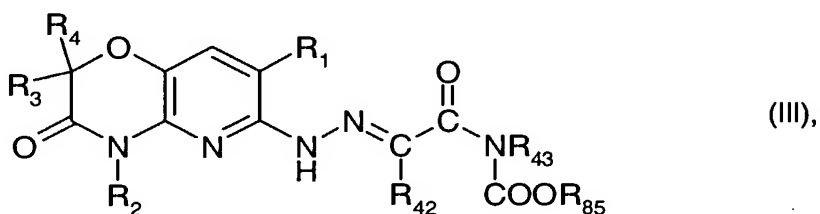
wherein R₄₂ and R₄₃ are as defined, to form the hydrazone derivative of formula IIk



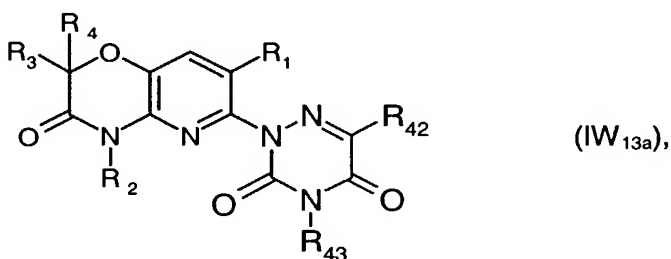
and further reacting that derivative with the chloroformic acid ester of formula XXXIVb



wherein R_{85} is $\text{C}_1\text{-C}_4$ alkyl, to form the compound of formula III



which is cyclised under basic conditions, for example in aqueous sodium or potassium hydroxide solution, to form the compound of formula IW_{13a}



or, in accordance with route n) in Reaction Scheme 9, the diazonium salt of formula Ilee may be coupled with the reagent of formula XXXVIIb



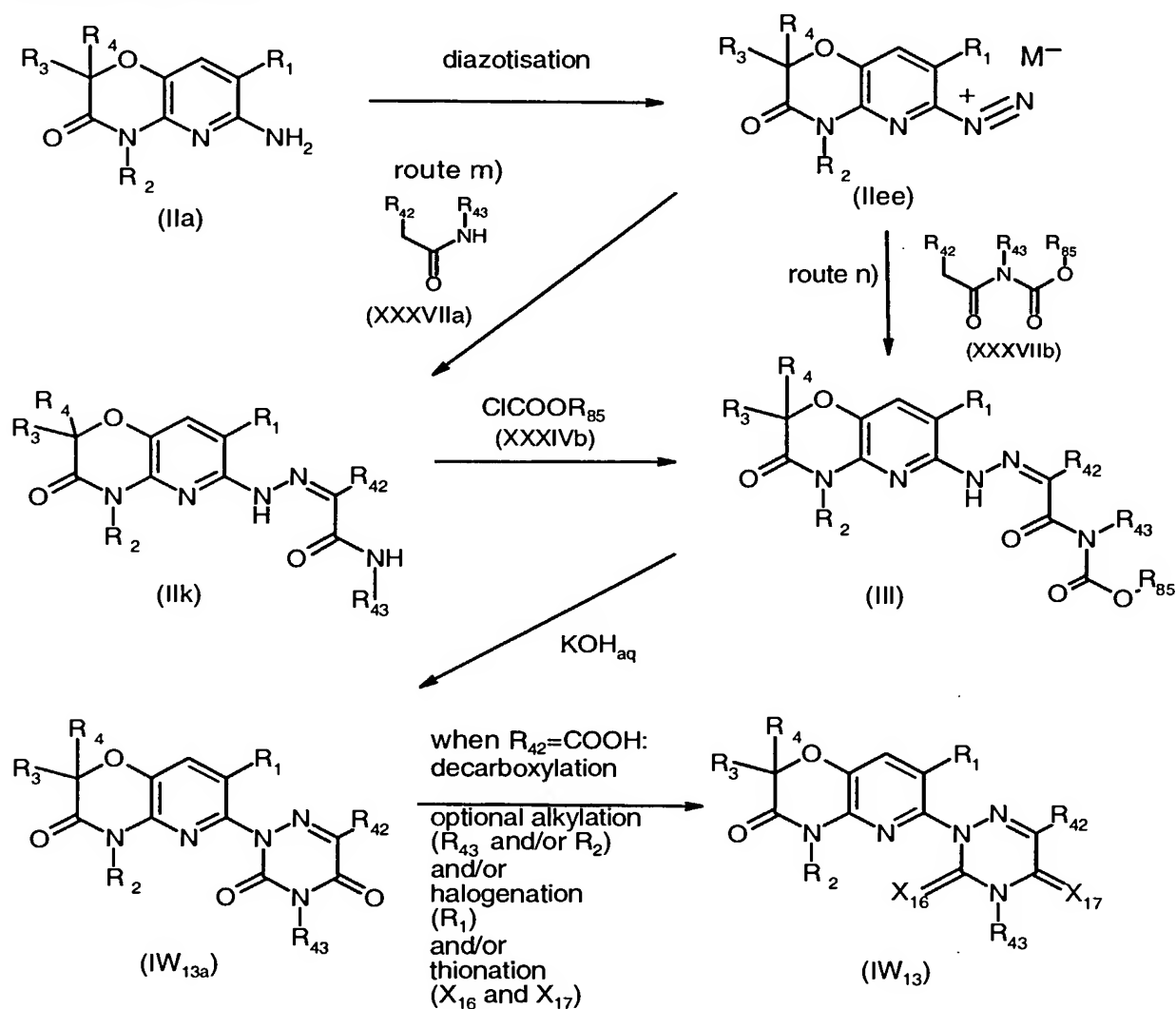
wherein R_{42} , R_{43} and R_{85} are as defined, to form the compound of formula III directly, which may then be cyclised analogously to route m), under basic conditions, to form the compound of formula IW_{13a}.

The resulting compounds of formula IW_{13a} wherein, for example, R_{42} is a carboxyl group may be converted into the compounds of formula IW₁₃ wherein R_{42} is hydrogen using standard decarboxylation methods, for example by heating in an aqueous mineral acid, e.g.

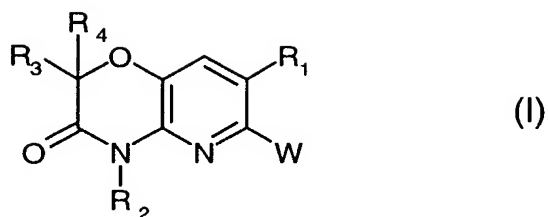
hydrochloric acid, or in the presence of a carboxylic acid, e.g. oxalic acid or thioglycolic acid, in an organic solvent, for example a halogenated hydrocarbon, e.g. chlorobenzene.

Furthermore, the compounds of formula IW_{13a} wherein R₄₃ and/or R₂ are hydrogen or R₁ is hydrogen may be further functionalised according to the definitions of R₁, R₂, R₄₃, X₁₆ and X₁₇ by means of alkylation and/or halogenation, as described under ab) and ac) in the former case and ae) in the latter case, or, when X₁₆ and X₁₇ in the compound of formula IW₁₃ are sulfur, by means of thionation as described under aa). Reaction Scheme 9 illustrates those reaction sequences.

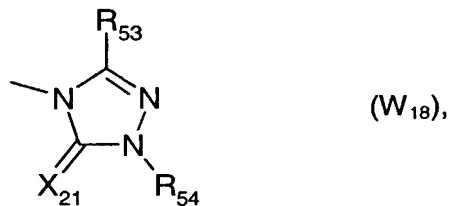
Reaction Scheme 9:



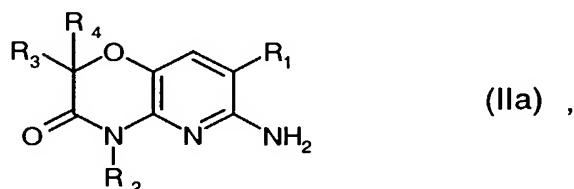
The process according to the invention for the preparation of compounds of formula I is carried out analogously to known processes, as described, for example, in EP-A-0 726 258, and comprises, for the preparation of those compounds of formula I



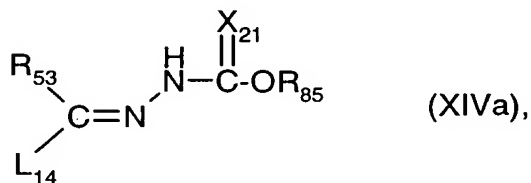
wherein R_1 , R_2 , R_3 and R_4 are as defined for formula I and W is a group W_{18}



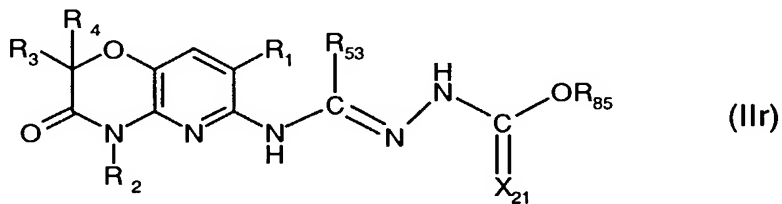
wherein R_{53} , R_{54} , and X_{21} are as defined for formula I, reacting a compound of formula IIa



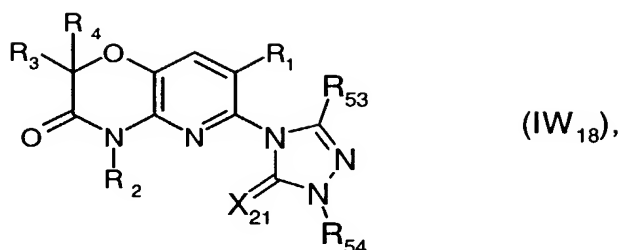
wherein R_1 , R_2 , R_3 and R_4 are as defined, with a hydrazinecarboxylic acid ester of formula XIVa



wherein R_{53} and X_{21} are as defined, R_{85} is C_1 - C_4 alkyl and L_{14} is a leaving group, for example halogen, e.g. chlorine or bromine, to form the compound of formula IIr



and heating that compound in the presence of an alkali metal hydroxide solution and cyclising that compound to form the compound of formula IW₁₈



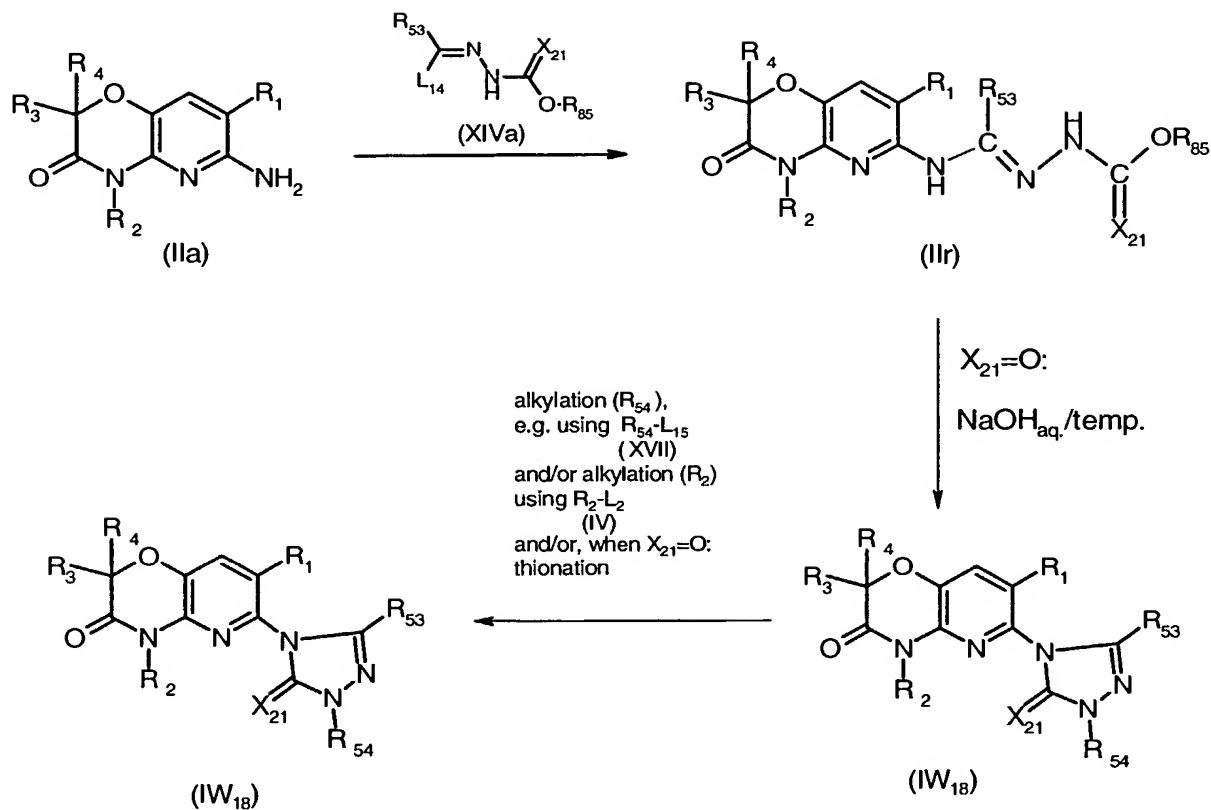
wherein R_1 , R_2 , R_3 , R_4 , R_{53} and X_{21} are as defined and R_{54} is hydrogen, and carrying out a further reaction with the alkylating reagent of formula XVII



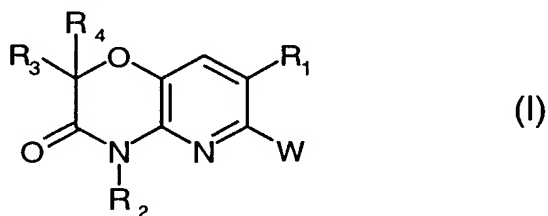
wherein R_{54} is C_1 - C_3 alkyl and L_{15} is a leaving group, for example halogen, especially chlorine, bromine or iodine, or a sulfonate, especially mesyloxy or tosyloxy, and/or, when R_2 is hydrogen, optionally carrying out a reaction, as described under ac) above, with the alkylating reagent of formula IV



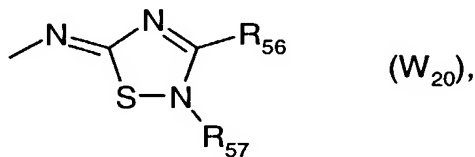
wherein R_2 is as defined for formula I with the exception of R_2 as hydrogen and L_2 is a leaving group, and/or, when X_{21} is oxygen, carrying out thionation as described under aa) above. Reaction Scheme 18 illustrates those reactions.

Reaction Scheme 18:

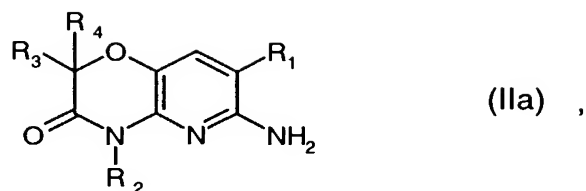
The process according to the invention for the preparation of compounds of formula I is carried out analogously to known processes, as described, for example, in J. Pestic. Sci. 18, 309 (1993), and comprises, for the preparation of those compounds of formula I



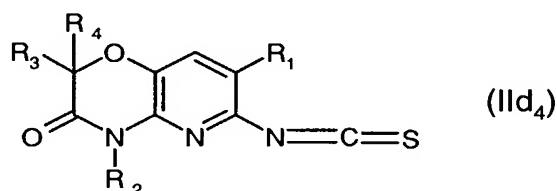
wherein R₁, R₂, R₃ and R₄ are as defined for formula I and W is a group W₂₀



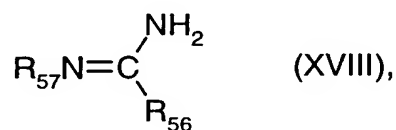
wherein R₅₆ and R₅₇ are as defined for formula I, first of all converting a compound of formula IIa



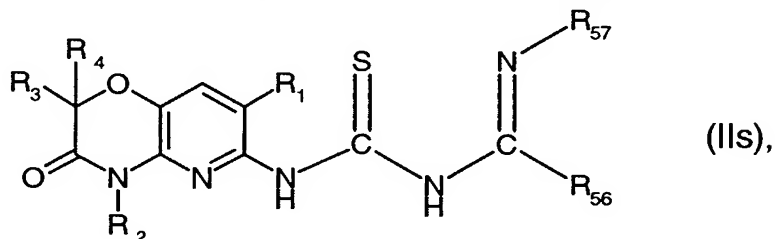
wherein R_1 , R_2 , R_3 and R_4 are as defined, for example using thiophosgene, into the isothiocyanate of formula IIId₄



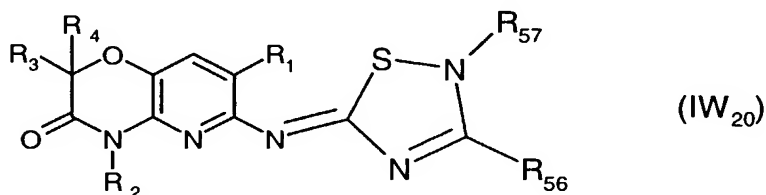
and then further reacting that isothiocyanate with an amidine derivative of formula XVIII



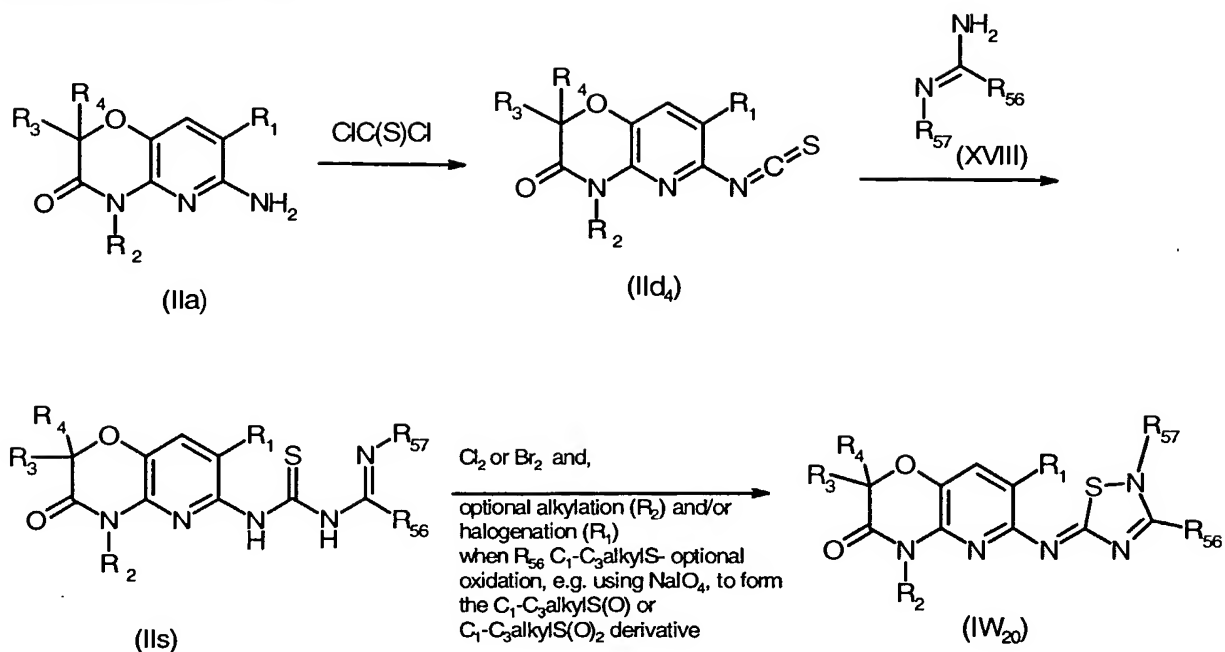
wherein R_{56} and R_{57} are as defined, to yield the compound of formula IIs



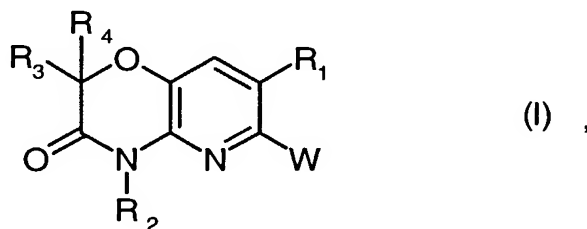
which, on treatment with chlorine or bromine, is cyclised to form the compound of formula IW₂₀



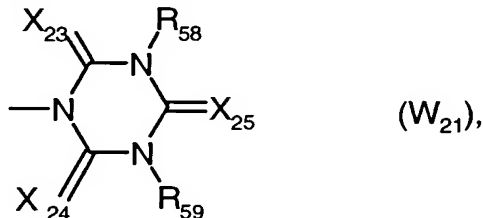
and is optionally alkylated (R_2) and/or halogenated (R_1) in accordance with standard processes as described under ac) and ae) and, when R_{56} is C_1 - C_3 alkylthio, is optionally oxidised using an oxidising agent, for example sodium periodate, to form the corresponding C_1 - C_3 alkylsulfinyl or C_1 - C_3 alkylsulfonyl derivative. Reaction Scheme 19 illustrates those reactions.

Reaction Scheme 19:

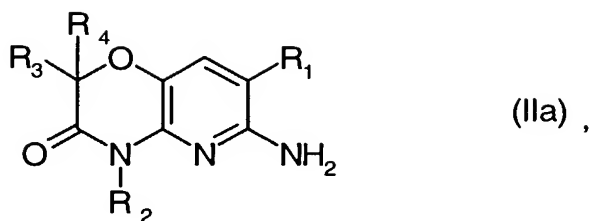
The process according to the invention for the preparation of compounds of formula I is carried out analogously to known processes, as described for example in DE 3516631 or DE 2718799, or in C. R. Hebd. Seances Acad. Sci., Ser. C (1976), 283, 491, for the preparation of those compounds of formula I



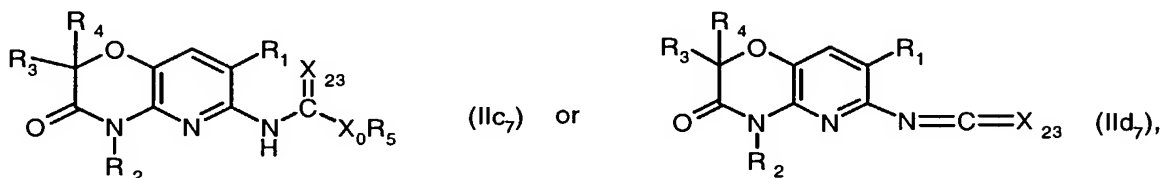
wherein R_1 , R_2 , R_3 and R_4 are as defined for formula I, and W is a group W_{21}



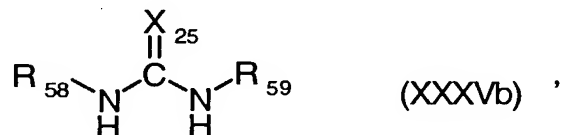
wherein R_{58} , R_{59} , X_{23} , X_{24} and X_{25} are as defined for formula I, first of all converting a compound of formula IIa



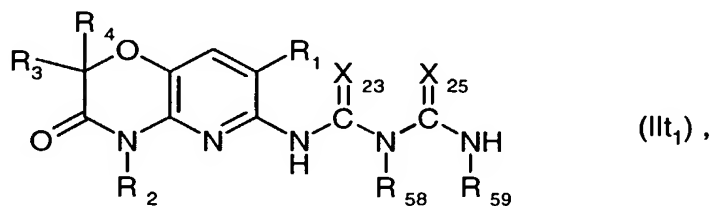
wherein R_1 , R_2 , R_3 and R_4 are as defined for formula I, either, according to Reaction Scheme 21, by reacting a compound of formula IIc₇ or IId₇



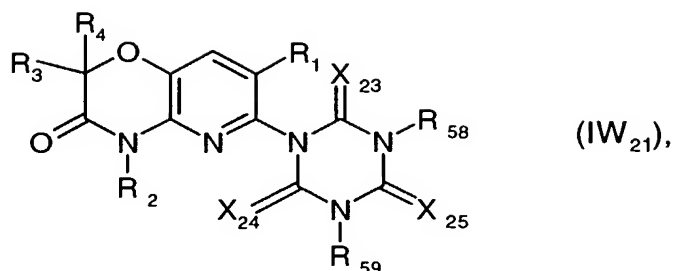
wherein R_1 , R_2 , R_3 , R_4 and X_{23} are as defined for formula I, X_0 is oxygen, and R_5 is C₁-C₄alkyl, with an urea of formula XXXVb



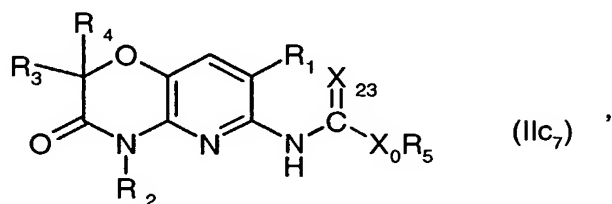
wherein R_{58} , R_{59} and X_{25} are as defined for formula I, in the presence of a base, for example a trialkylamine, and a suitable solvent, for example a chlorinated hydrocarbon, e.g. chlorobenzene, or an amide, e.g. DMF or NMP, to thereby yield the compound of formula IIIt₁



wherein R_1 , R_2 , R_3 , R_4 , R_{58} , R_{59} , X_{23} and X_{25} are as defined, and then cyclising that compound in the presence of a carbonyl equivalent like phosgene, diphosgene, ethylchloroformate (compound of formula VIc), carbonyldiimidazol (CDI), carbonylbistriazol, to form the compound of formula IW₂₁



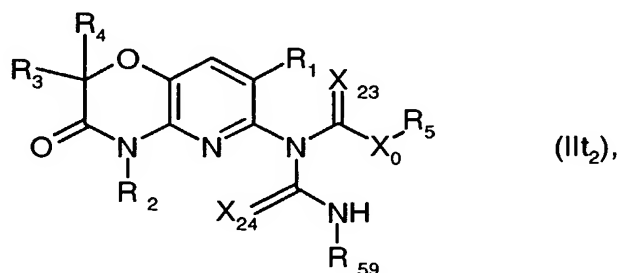
or according to Reaction Scheme 21, reacting a compound of formula IIc₇



wherein R₁, R₂, R₃, R₄ and X₂₃ are as defined for formula I, X₀ is oxygen, and R₅ is C₁-C₄alkyl, firstly in a suitable solvent, for example a chlorinated hydrocarbon, e.g. chlorobenzene, or an amide, e.g. DMF or NMP, with an isocyanate or an isothiocyanate of the formula XIo



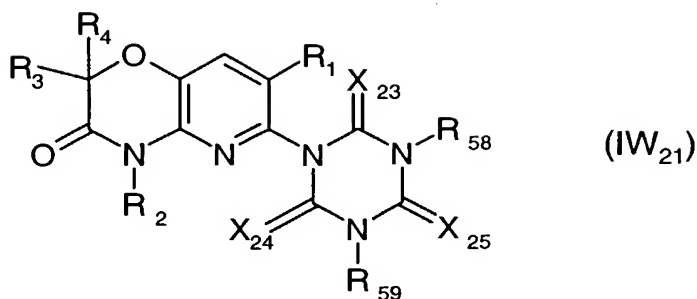
wherein R₅₉ and X₂₄ are as defined for formula I, to thereby yield the compound of formula II_{t2}



wherein R₁, R₂, R₃, R₄, R₅, R₅₉, X₂₃ and X₂₄ are as defined, X₀ is oxygen, and R₅ is C₁-C₄alkyl, and then cyclising that compound in the presence of an isocyanate or an isothiocyanate of formula XIp



wherein R₅₈ and X₂₅ are as defined for formula I, to form the compound of formula IW₂₁



The compound of formula IW₂₁ may, optionally, be further functionalised according to the definitions of R₁, R₂, R₅₈, R₅₉, X₂₃, X₂₄ and X₂₅ in analogous manner to that described under aa), ac) or ae).

For example, the compound of formula IW₂₁, wherein R₅₈ and/or R₅₉ are hydrogen, can be further reacted, in analogous manner to that described under ac), with an alkylating reagent of formula XVc and/or XVd

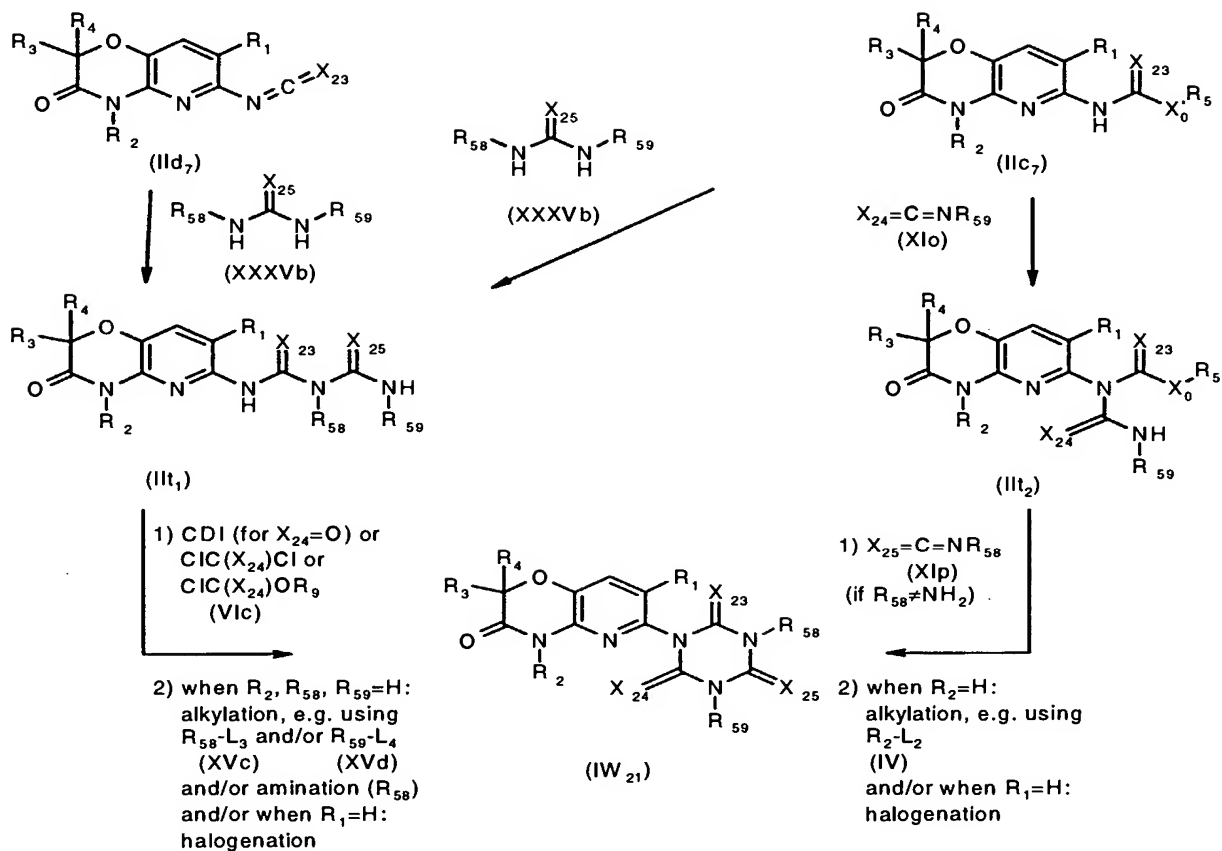


wherein R₅₈ and R₅₉ are as defined for formula I with the exception of R₅₈ and R₅₉ as hydrogen, and L₃ and L₄ are each a leaving group, for example halogen, especially chlorine, bromine or iodine, or a sulfonate, especially mesyloxy or tosyloxy, in the presence of a suitable base to form the compound of formula IW₂₁, wherein R₅₈ and/or R₅₉ are C₁-C₃alkyl or C₁-C₃haloalkyl. Optionally, the compound of formula IW₂₁, wherein R₂ is hydrogen, and R₅₈ and R₅₉ are other than hydrogen can be alkylated in the presence of a base, for example an alkali metal carbonate, e.g. potassium carbonate as acid-binding agent, with the reagent of formula IV

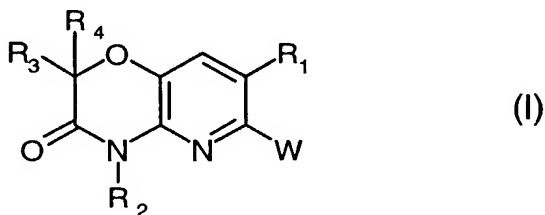


wherein R₂ is as defined for formula I with the exception of R₂ as hydrogen, and L₂ is a leaving group, for example halogen, e.g. chlorine, bromine or iodine, or sulfonate, e.g. mesyloxy or tosyloxy.

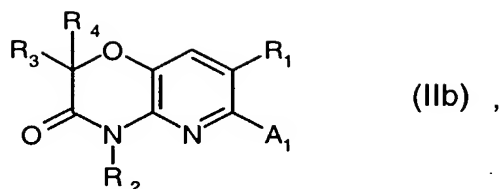
Reaction Scheme 21:



The process according to the invention for the preparation of compounds of formula I according to variant c) and Reaction Scheme 1c) is carried out analogously to known processes and comprises, for the preparation of those compounds of formula I



wherein R₁, R₂, R₃ and R₄ are as defined for formula I and W is a group W₁ to W₂₁ (C-N-linked ring systems), reacting a compound of formula IIb

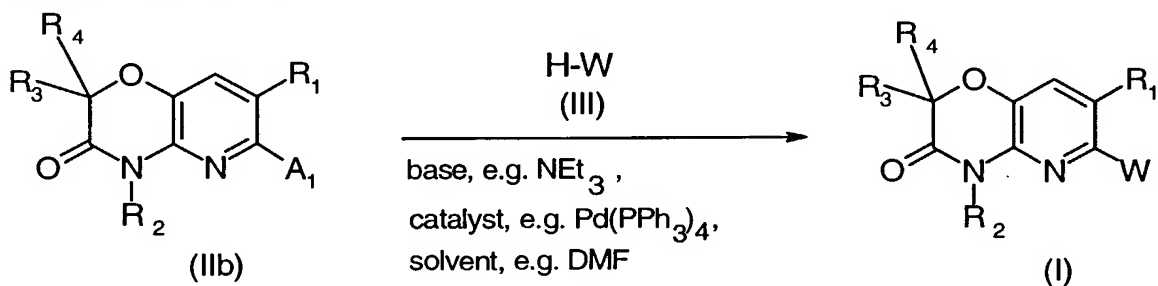


wherein R_1 , R_2 , R_3 and R_4 are as defined and A_1 is a leaving group, for example halogen, especially fluorine, chlorine or bromine, sulfonyl, especially methylsulfonyl, sulfonate, especially trifluoromethylsulfonyloxy, methylsulfonyloxy or phenylsulfonyloxy, or nitro, with an N-heterocyclic compound of formula III

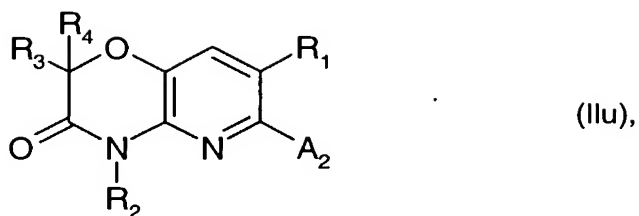


wherein W is a group W_1 to W_{21} , in the presence of a base, for example a trialkylamine, especially triethylamine, a carbonate, especially sodium and potassium carbonate, or also caesium fluoride, in the presence of one or more suitable catalysts, for example metal catalysts, especially palladium catalysts, e.g. tetrakis(triphenylphosphine)palladium ($\text{Pd}(\text{PPh}_3)_4$), bis(triphenylphosphine)palladium(II) dichloride ($\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$) or palladium(II) acetate ($\text{Pd}(\text{OAc})_2$), and/or copper iodide, and further catalytic additives, for example various phosphine ligands, e.g. biphenyl-2-bis-tert-butylphosphine, and in the presence of a suitable diluent, for example an aromatic hydrocarbon, e.g. one of the xylene isomers, or an amide, e.g. NMP or DMF, as illustrated in Reaction Scheme 1c.

Reaction Scheme 1c:

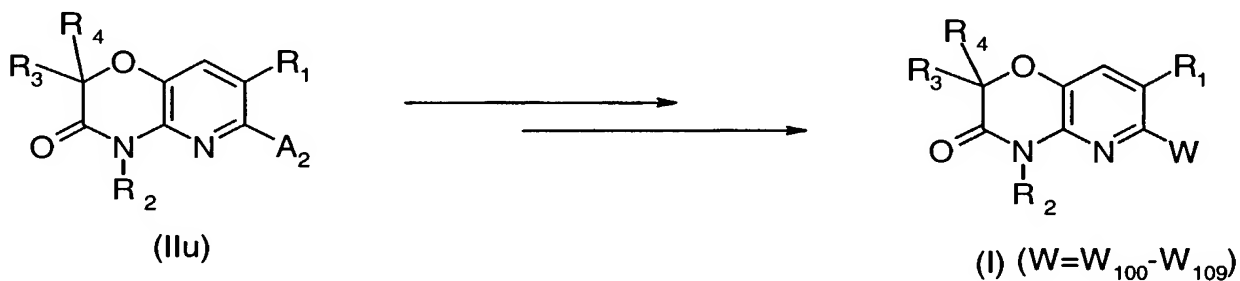


The process according to the invention for the preparation of compounds of formula I wherein W is a group W_{100} to W_{109} (C-C-linked ring systems) is carried out, for example, starting from compounds of formula IIu

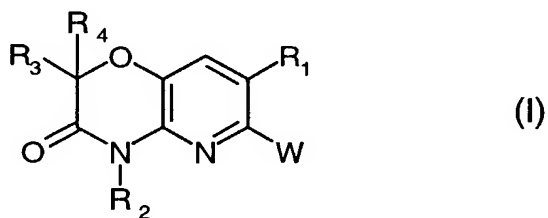


wherein R_1 to R_4 are as defined for formula I and A_2 is methyl, ethyl, ethynyl, cyano, formyl, acyl, carboxy or C_1 - C_4 alkoxycarbonyl, according to variant d) and Reaction Scheme 1d

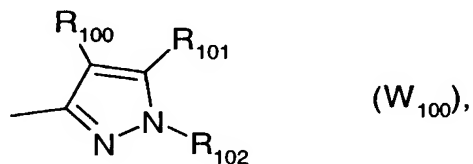
Reaction Scheme 1d:



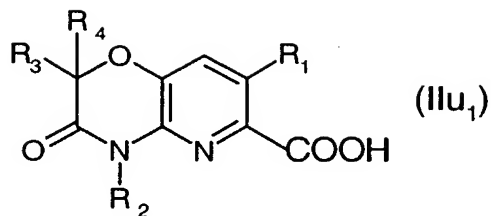
or analogously to known processes, as described, for example, in EP-A-0 839 808, WO 96/01254 and WO 98/21199, and comprises, for the preparation of those compounds of formula I



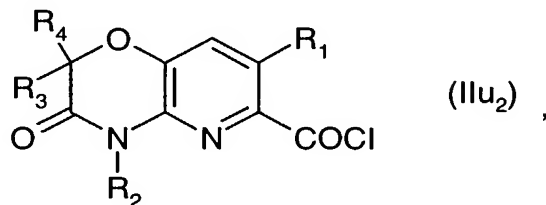
wherein R_1 , R_2 , R_3 and R_4 are as defined for formula I and W is a group W_{100}



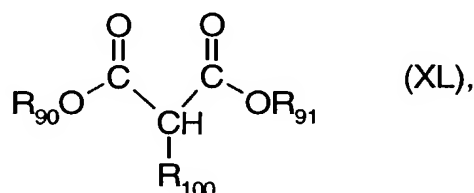
wherein R_{100} is hydrogen, chlorine or bromine, R_{101} is difluoromethoxy and R_{102} is as defined for formula I, converting a compound of formula IIu₁



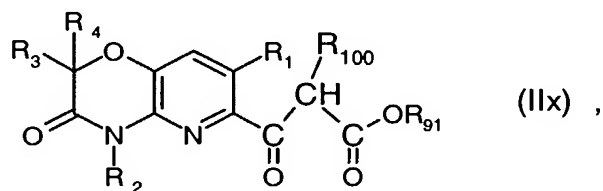
using standard processes, for example using thionyl chloride, oxalyl chloride or phosgene, into the activated form (acid chloride) of formula IIu₂



the substituents R₁, R₂, R₃ and R₄ in the compounds of formulae IIu₁ and IIu₂ being as defined, and reacting the latter compound with a malonic acid ester of formula XL



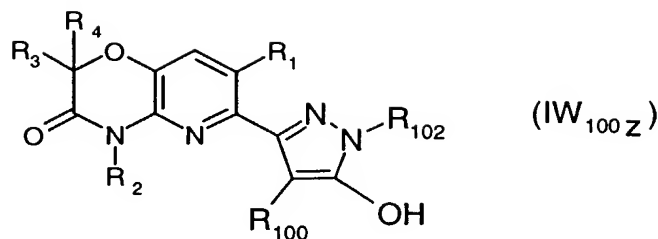
wherein R₉₀ is hydrogen, a sodium, potassium or magnesium cation, trimethylsilyl or C₁-C₄alkyl, R₉₁ is C₁-C₄alkyl and R₁₀₀ is as defined for formula I, in the presence of a suitable base, for example an alkylamine, e.g. triethylamine, and an inert solvent, for example an amide, e.g. DMF, and subsequent hydrolysis to form the keto ester of formula IIx



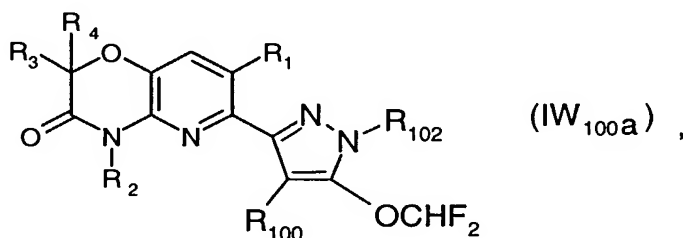
then cyclising that keto ester with a hydrazine derivative of formula XLI



wherein R₁₀₂ is as defined for formula I, to form the pyrazolone derivative of formula IW_{100z}



and finally subjecting that derivative to a freonisation reaction, for example using chlorodifluoromethane or bromodifluoromethane in the presence of a suitable base, for example an alkali metal hydroxide, especially sodium hydroxide, or a carbonate, especially potassium carbonate, and in a suitable solvent, for example an ether, e.g. tetrahydrofuran or dioxane, or water, or in a two-phase system containing water and a chlorinated hydrocarbon at temperatures of from -10° to 110°C or advantageously in a closed system under slight overpressure and, when R₁₀₀ is hydrogen, optionally to a halogenation reaction, for example using halogen, e.g. chlorine or bromine, or using sulfonyl halide, e.g. sulfonyl chloride, to thereby yield the compound of formula IW_{100a}



R₁, R₂, R₃, R₄ and R₁₀₂ in the compounds of formulae IW_{100z} being IW_{100a} as defined and R₁₀₀ being hydrogen or halogen, and, optionally, further functionalising that compound according to the definitions of R₁, R₂, R₁₀₀ and R₁₀₂ given for formula I in accordance with standard methods.

Compounds of formula IW_{100a} wherein R₂ is hydrogen may, for example, be alkylated, according to process variant ac), using an appropriate alkylating reagent of formula IV



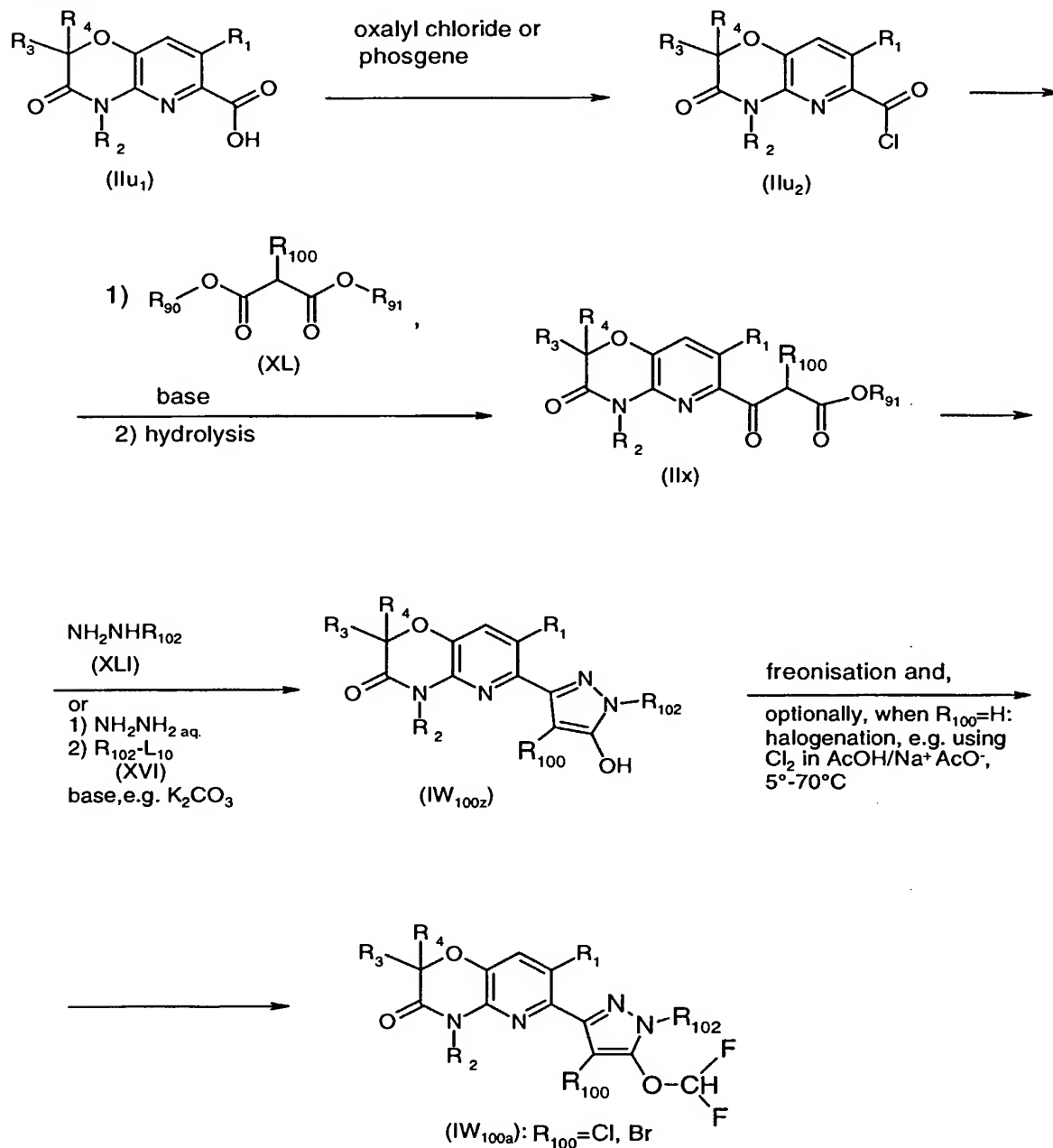
wherein R₂ is as defined for formula I with the exception of R₂ as hydrogen, and L₂ is a leaving group; or compounds of formula IW_{100a} wherein R₁ is hydrogen may, for example, be halogenated according to process variant ae), using a suitable halogenating reagent. The halogenation reaction can advantageously be carried out 'in situ', following on from the freonisation reaction. Chlorination is carried out, for example, by passing an equimolar amount or slight excess of chlorine gas into a suitable solvent system, for example a carboxylic acid, e.g. acetic acid, in the presence of a weak base, for example sodium

acetate, at temperatures of from 5° to 70°C. By that means, compounds of formula IW_{100a} wherein R₁₀₀ is chlorine and R₁ is hydrogen are obtained selectively.

When the above halogenation reaction is carried out using an excess of halogenating reagent, it is possible to obtain, from compounds of formula IW_{100z} wherein R₁ is hydrogen, the corresponding dihalogenated compound of formula IW_{100a} wherein R₁ and R₁₀₀ are halogen, especially chlorine or bromine.

Reaction Scheme 11 illustrates those reactions.

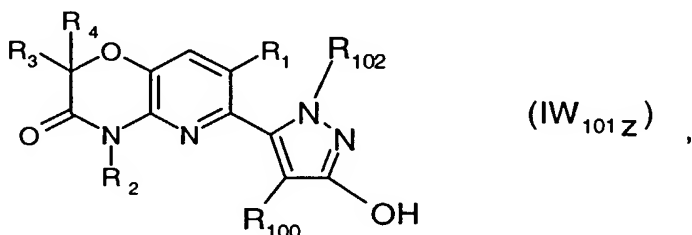
Reaction Scheme 11:



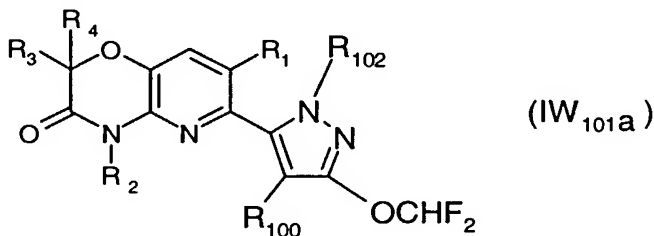
If the keto ester of formula IIx is reacted with hydrazine (compound of formula XLI wherein R_{102} is hydrogen) there is formed the pyrazolone derivative of formula IW_{100z} wherein R_{102} is hydrogen, which, on subsequent alkylation using the reagent of formula XVI



wherein R_{102} is as defined for formula I with the exception of R_{102} as hydrogen, and L_{10} is a leaving group, for example halogen, especially chlorine, bromine or iodine, or sulfonate, especially mesyloxy or tosyloxy, in addition to the compound of formula IW_{100z}, wherein R_{102} is as defined, also yields the isomeric pyrazolone derivative of formula IW_{101z}

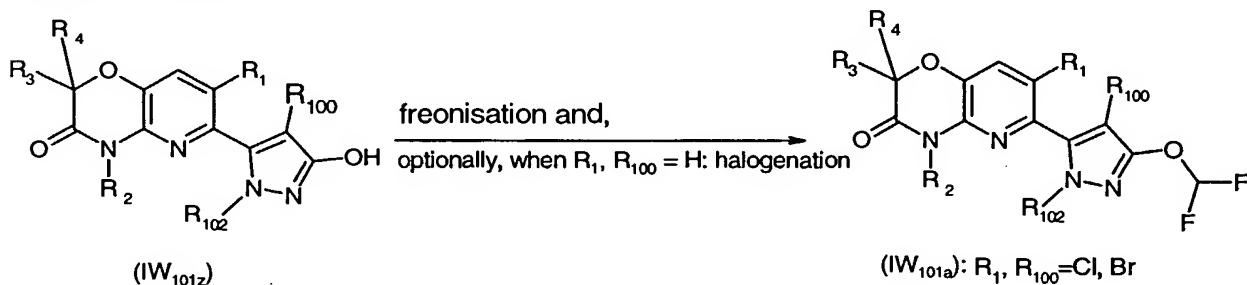


and, by means of a freonisation reaction, and when R_{100} is hydrogen optionally by means of a halogenation reaction, the corresponding isomeric compound of formula IW_{101a}

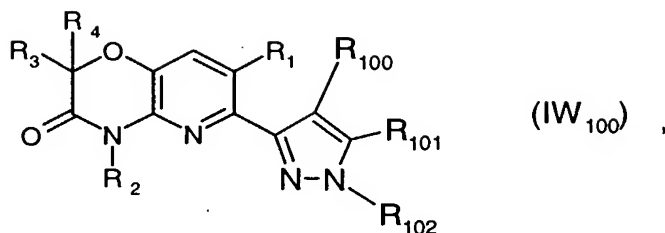


(Reaction Scheme 12). That compound may optionally be further functionalised according to the definitions of R_1 , R_2 , R_{100} and R_{102} for formula I by means of standard methods.

Reaction Scheme 12:

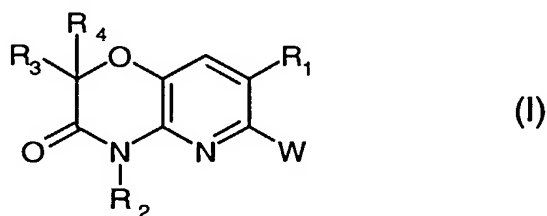


Further synthesis processes for the preparation of compounds of formula IW₁₀₀

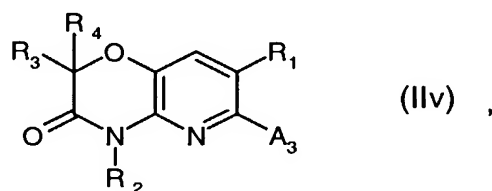


wherein R₁, R₂, R₃, R₄, R₁₀₀ and R₁₀₂ are as defined for formula I and R₁₀₁ is trifluoromethyl (compound of formula IW_{100b}), cyano (compound of formula IW_{100c}), or methylthio, methylsulfinyl or methylsulfonyl (compound of formula IW_{100d}), or R₁₀₁ and R₁₀₂ together form a C₃-C₅alkylene bridge (compound of formula IW_{100e}), may be carried out in analogous manner to that described, for example, in WO 98/21199 and EP-A-0 839 808.

The process according to the invention for the preparation of compounds of formula I according to variant e) and Reaction Scheme 1e is carried out analogously to known processes and comprises, for the preparation of those compounds of formula I



wherein R₁, R₂, R₃, R₄ and W are as defined for formula I, reacting a compound of formula IIv



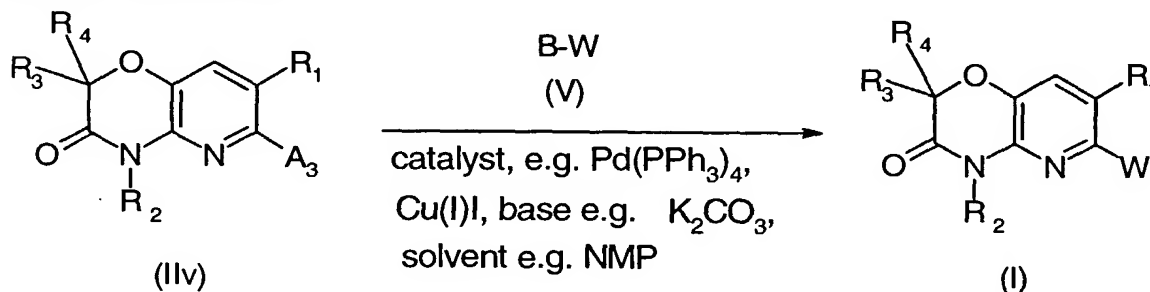
wherein R₁, R₂, R₃ and R₄ are as defined and A₃ either is a leaving group, for example halogen, especially chlorine or bromine, or sulfonate, especially trifluoromethylsulfonyloxy, or is a trialkylstannyl or boronic acid group, with a corresponding heterocyclic compound of formula V



wherein W is as defined for formula I and B, complementarily to A₃ in the compound of formula IIv, either is a trialkylstannyl or boronic acid group or is a leaving group, for example halogen, especially chlorine or bromine, or sulfonate, especially trifluoromethylsulfonyloxy, in the presence of a metal catalyst from the noble metals group that is suitable for C-N or C-

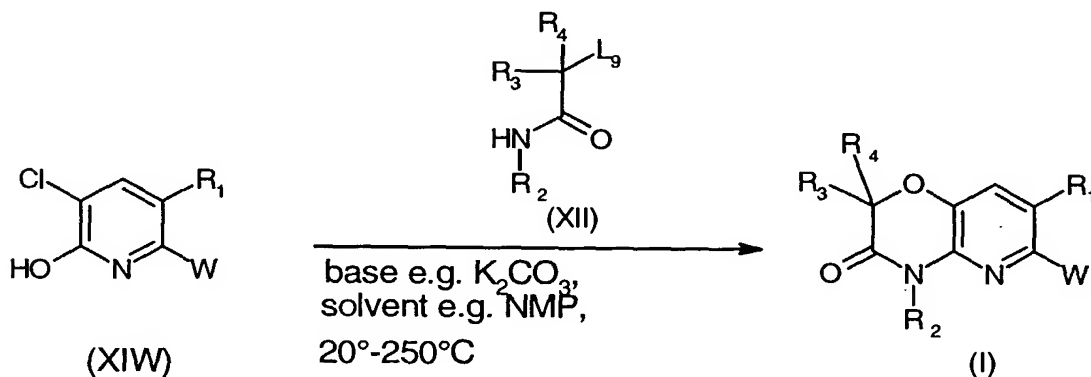
C linkages for example palladium, in the presence of a suitable activation ligand, for example triphenylphosphine or 2-(di-tert-butyl)diphenylphosphine, in the presence of a copper salt, for example copper iodide, in the presence of a suitable base, for example a trialkylamine, especially triethylamine, or a carbonate, especially sodium or potassium carbonate, and in a suitable solvent, for example N-methylpyrrolidone (NMP) or N,N-dimethylformamide (DMF) (Reaction Scheme 1e).

Reaction Scheme 1e:

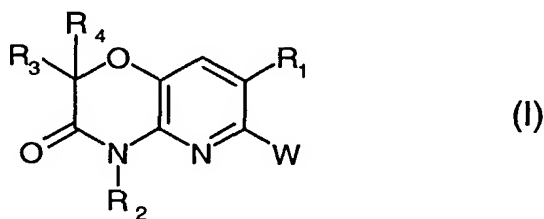


The process according to the invention for the preparation of compounds of formula I according to variant f) and Reaction Scheme 1f

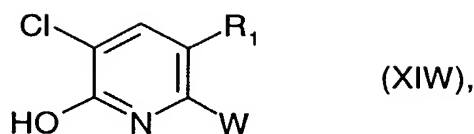
Reaction Scheme 1f:



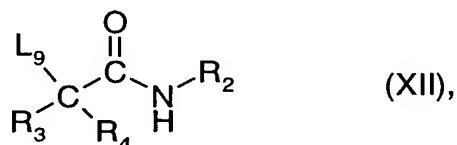
is carried out analogously to known processes and comprises, for the preparation of those compounds of formula I



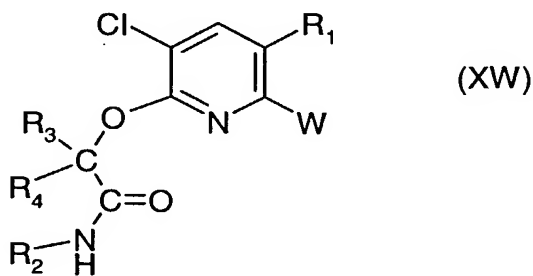
wherein R_1 , R_2 , R_3 , R_4 and W are as defined for formula I, but W is especially a group W_{100} , reacting a compound of formula XIW



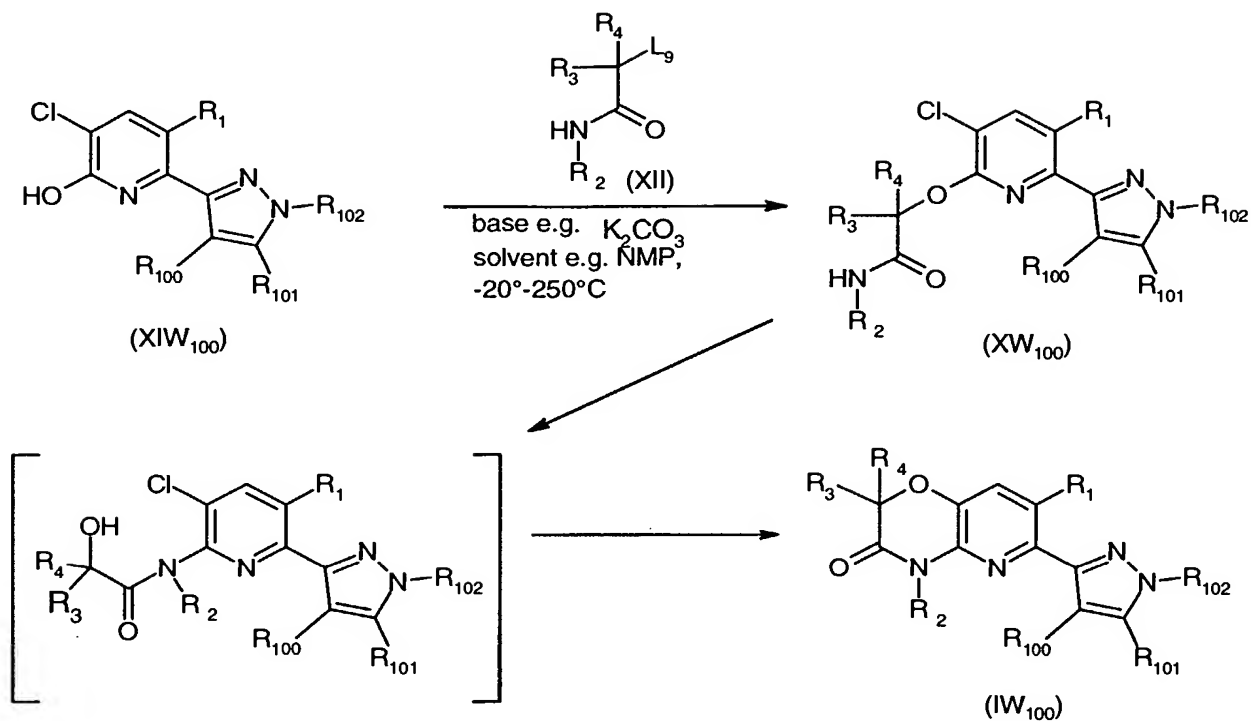
wherein R_1 and W are as defined for formula I, but W is especially a group W_{100} (compound of formula XIW_{100} in Reaction Scheme 22), in the presence of a base, for example a carbonate, especially sodium or potassium carbonate, and an inert organic solvent, for example N-methylpyrrolidone, at temperatures of from -20° to 250°C and normal pressure or under slight overpressure, but preferably at the boiling point of the solvent in question, with a compound of formula XII



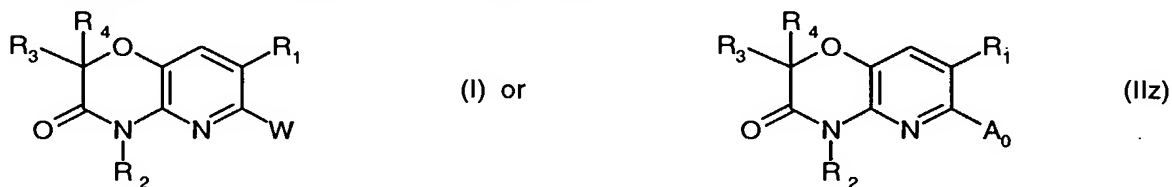
wherein R_2 , R_3 and R_4 are as defined for formula I, and L_9 is a leaving group, for example halogen, especially chlorine or bromine, or sulfonate, especially mesyloxy, tosyloxy or trifluoromethanesulfonyloxy, to yield the compound of formula XW



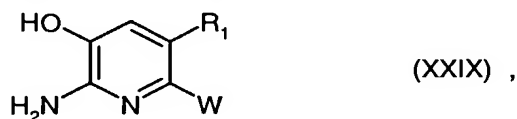
and rearranging and cyclising that compound in the presence of base, for example a carbonate, especially sodium or potassium carbonate, and an inert organic solvent, for example an amide, e.g. N-methylpyrrolidone, at temperatures of from 20° to 250°C and under normal pressure or under slight overpressure but preferably at the boiling point of the solvent used. The above reaction sequence consisting of nucleophilic substitution, subsequent rearrangement and ring-closure reaction may proceed in the same reaction vessel, as a so-called 'one-pot reaction', as illustrated in Reaction Scheme 22.

Reaction Scheme 22:

The process according to the invention for the preparation of compounds of formula I according to variant g) and Reaction Scheme 1g is carried out analogously to known processes, as described, for example, in Acta Chimica Scandinavica 23, 2322 (1969), and comprises, for the preparation of those compounds of formula I or IIz



wherein R₁, R₃ and R₄ are as defined for formula I, R₂ is especially hydrogen, W is especially a group W₁₄ or W₁₀₀-W₁₀₉, and A₀ is especially hydrogen, methyl, ethyl, fluorine, chlorine, bromine or carboxy, condensing a compound of formula XXIX

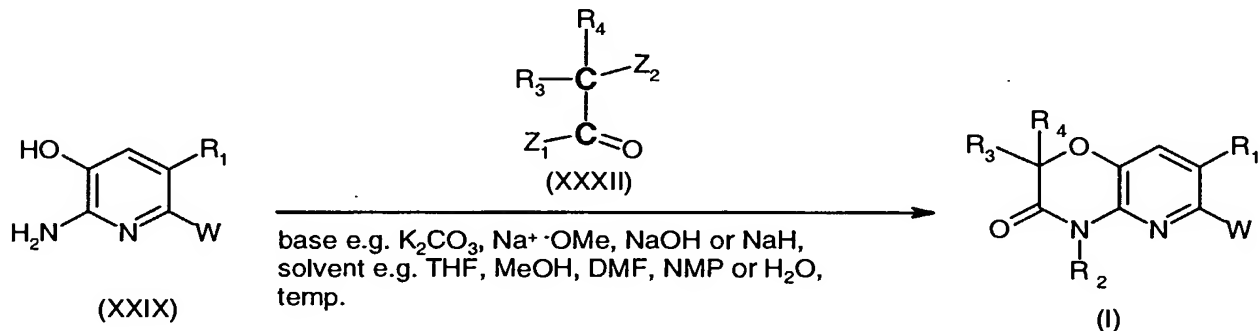


wherein R₁ and W are as defined, with an acetic acid derivative of formula XXXII

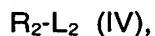


wherein R_3 and R_4 are as defined, Z_1 is a C_1 - C_4 alkoxy group or a leaving group, for example chlorine or bromine, and Z_2 is a leaving group, for example chlorine or bromine, or a sulfonate, for example mesyloxy or tosyloxy, in the presence of a suitable base, for example an alkali metal carbonate, e.g. potassium carbonate, an alcoholate, e.g. sodium methanolate or potassium tert-butanolate, a hydride, e.g. sodium hydride, or a hydroxide, e.g. sodium, potassium or barium hydroxide, and a suitable solvent, for example an alcohol, e.g. methanol, ethanol or methyl Cellosolve, an ether, e.g. tetrahydrofuran, diethoxymethane or dioxane, an aromatic hydrocarbon, e.g. toluene, a nitrile, e.g. acetonitrile, an amide, e.g. DMF or NMP, a sulfoxide, e.g. dimethyl sulfoxide, or water.

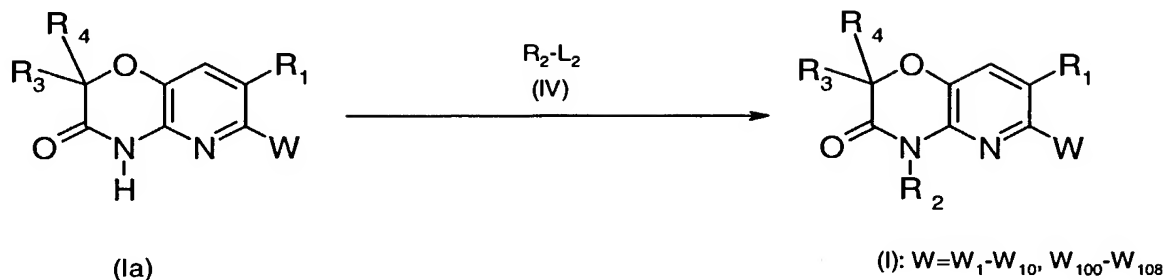
Reaction Scheme 1g:



The process according to the invention for the preparation of compounds of formula I comprises, in accordance with variant a), reacting compounds of formula Ia, wherein R_1 , R_3 , R_4 and W are as defined for formula I, with an appropriate alkylating reagent of formula IV

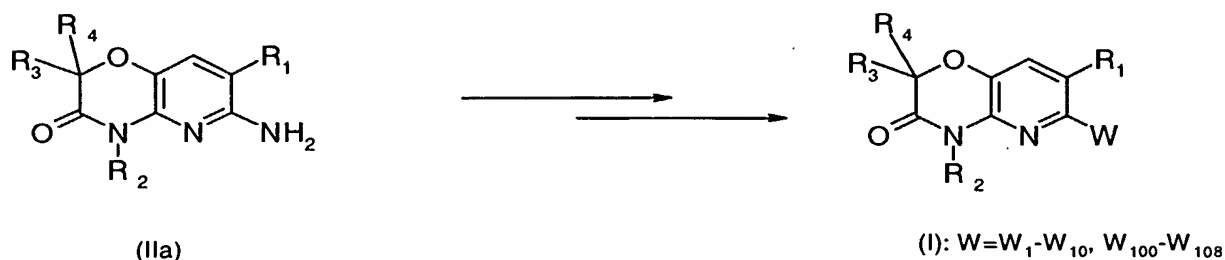


wherein R_2 is as defined for formula I with the exception of R_2 as hydrogen, and L_2 is a leaving group, in the presence of a base and a suitable solvent, as illustrated in Reaction Scheme 1a₀:

Reaction Scheme 1a₀:

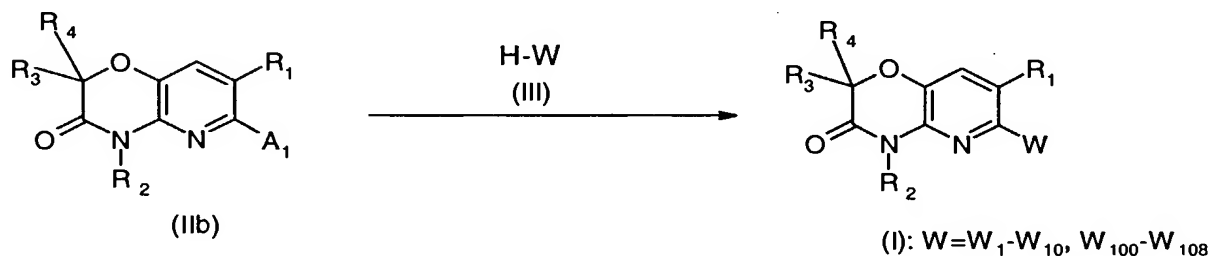
or

variant b), converting compounds of formula IIa, wherein R₁ to R₄ are as defined for formula I, analogously to known one- or multi-stage synthesis processes, into the corresponding cyclic ring systems W₁ to W₁₀ or W₁₀₀ to W₁₀₈ in a multi-stage synthesis according to Reaction Scheme 1b₀:

Reaction Scheme 1b₀:

or

variant c), reacting compounds of formula IIb, wherein R₁ to R₄ are as defined for formula I and A₁ is a leaving group, for example fluorine, chlorine, bromine, methylsulfonyl, trifluoromethylsulfonyloxy, methylsulfonyloxy, phenylsulfonyloxy or nitro, in the presence of a base and one or more suitable catalysts and a suitable diluent, with a cyclic compound of formula III, wherein W is as defined for formula I, according to Reaction Scheme 1c₀:

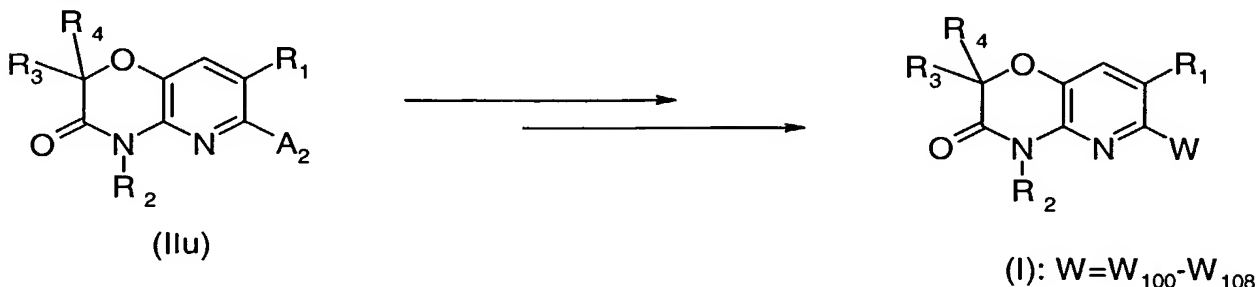
Reaction Scheme 1c₀:

or

variant d), converting compounds of formula IIu, wherein R₁ to R₄ are as defined for formula I and A₂ is methyl, cyano, formyl, acyl, carboxyl or C₁-C₄alkoxycarbonyl, analogously to known one- or multi-stage synthesis processes, according to Reaction

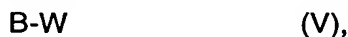
Scheme 1d₀, into the corresponding cyclic C-C-linked ring systems of formula I wherein W is W₁₀₀ to W₁₀₈:

Reaction Scheme 1d₀:



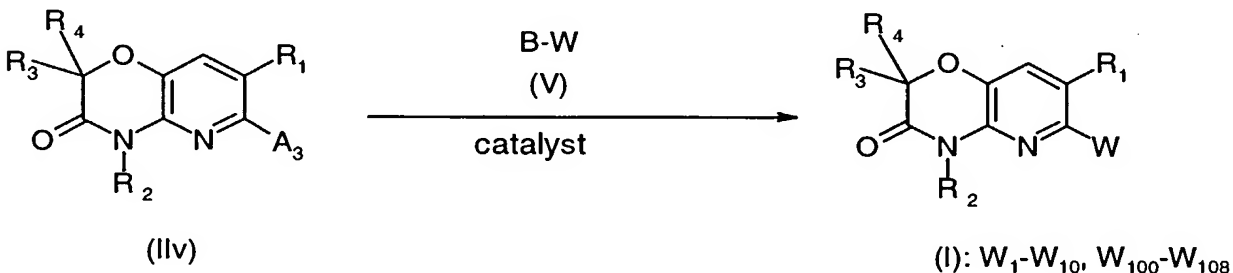
or

variant e), reacting compounds of formula IIv, wherein R₁ to R₄ are as defined for formula I and A₃ either is a leaving group, for example chlorine, bromine or trifluoromethylsulfonyloxy or is a trialkylstannyl or boronic acid group, with a corresponding heterocyclic compound of formula V



wherein W is as defined above for W₁ to W₁₀ or W₁₀₀ to W₁₀₈, and B, complementarily to A₃, either is a trialkylstannyl or boronic acid group, or is a leaving group, for example chlorine, bromine or trifluoromethylsulfonyloxy, in the presence of a metal catalyst from the noble metals group that is suitable for C-N or C-C linkages, for example palladium, in the presence of a suitable activation ligand, for example triphenylphosphine or 2-(di-tert-butyl)diphenylphosphine, in the presence of a copper salt, for example copper iodide, and in the presence of a suitable base, for example potassium carbonate or triethylamine, in a suitable inert solvent, for example N-methylpyrrolidone or dimethylformamide, according to Reaction Scheme 1e₀:

Reaction Scheme 1e₀:

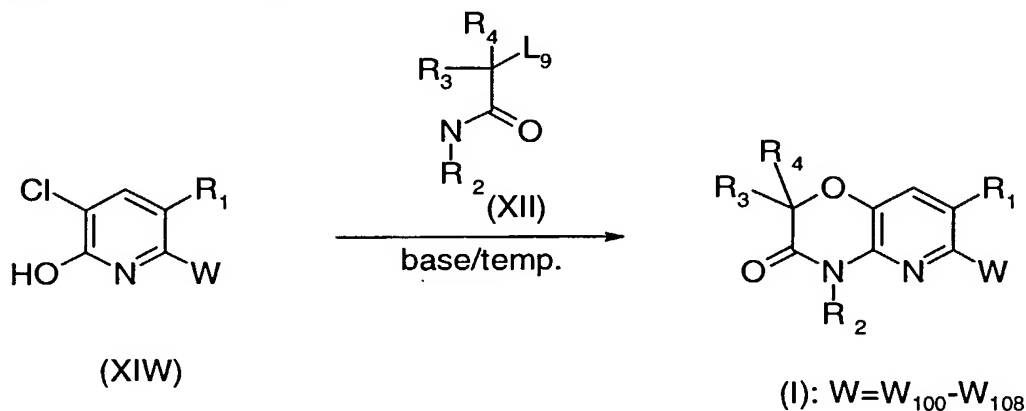


or

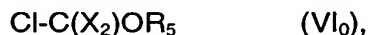
variant f), reacting compounds of formula XIW, wherein R₁ is as defined for formula I, and W is especially a group W₁₀₀, in the presence of a base and an inert solvent at elevated

temperatures, with a compound of formula XII, wherein R_2 to R_4 are as defined for formula I and L_9 is a leaving group, as illustrated in Reaction Scheme 1f₀:

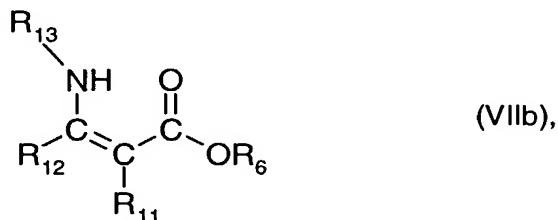
Reaction Scheme 1f₀:



The process according to the invention described under variant b) and in Reaction Scheme 1b for the preparation of compounds of formula I wherein W is a group W₁ is carried out analogously to known processes, as described, for example, in WO 99/52892 and WO 98/27083, and comprises converting a compound of formula IIa (Reaction Scheme 1₀), using a suitable reagent, for example oxalyl chloride, phosgene or thiophosgene, or using a reagent of formula VI₀



wherein X_2 is as defined for formula I and R_5 is C₁-C₄alkyl, into an intermediate of formula II_d or II_{c0}, respectively, and then condensing that intermediate with the corresponding enamine of formula VII_b



wherein R_{11} , R_{12} and R_{13} are as defined for formula I and R_6 is C₁-C₄alkyl, in the presence of from 0.1 to 1.5 equivalents of a suitable base in an inert solvent to form the group W₁ and then, optionally, in an additional standard conversion reaction, either

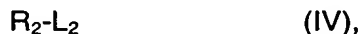
aa) when X_1 and/or X_2 are sulfur, treatment with a thionating reagent, for example Lawesson's reagent, is carried out, or

ab) when R_{13} is hydrogen and X_2 is oxygen, reaction with an alkylating reagent of formula IX



wherein R_{13} is as defined above with the exception of R_{13} as hydrogen, and L_1 is a leaving group, is carried out, and/or

ac) when R_2 is hydrogen, reaction, according to process variant a), with an appropriate alkylating reagent of formula IV



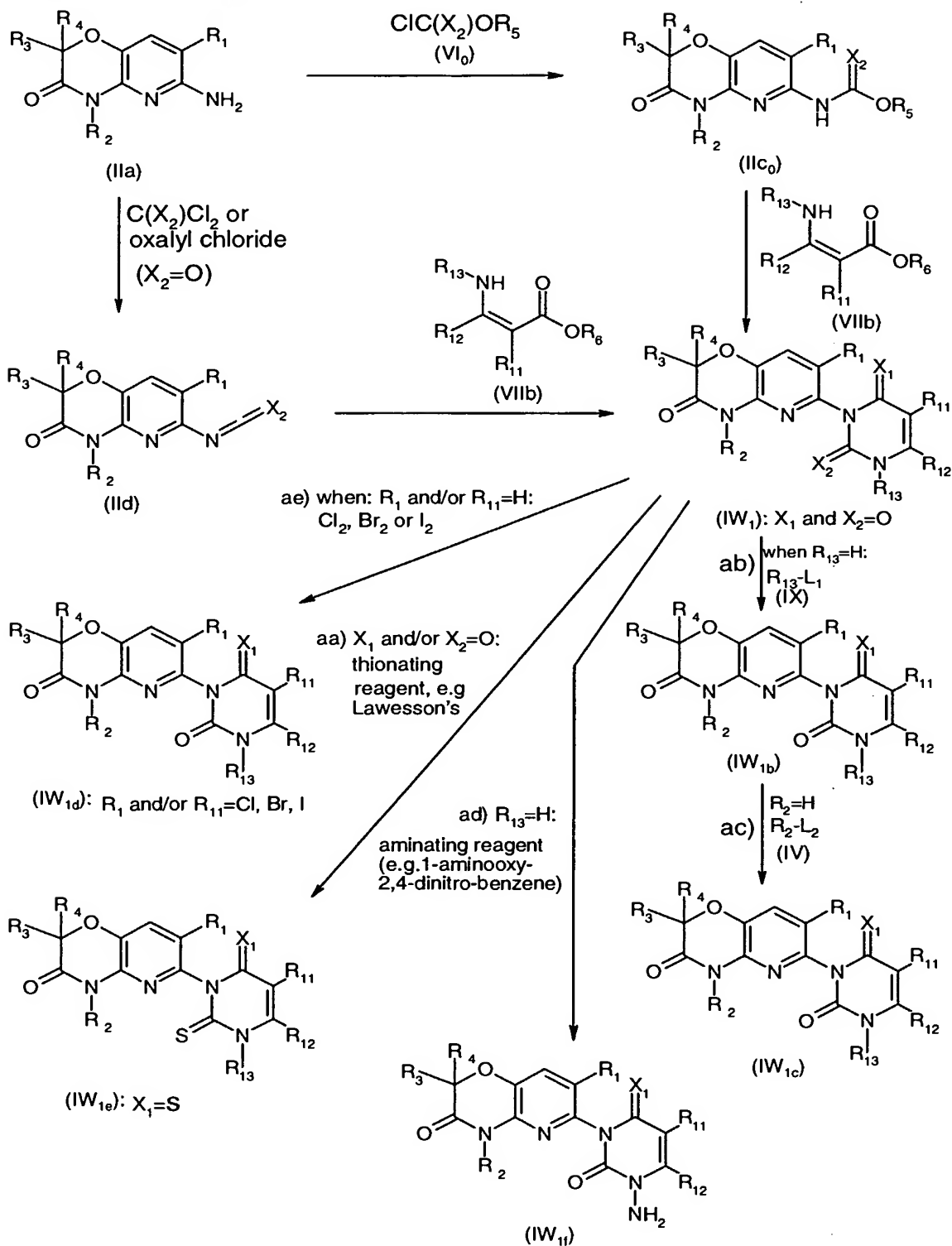
wherein R_2 is as defined for formula I with the exception of R_2 as hydrogen, and L_2 is a leaving group, for example chlorine, bromine, methylsulfonyloxy or phenylsulfonyloxy, is carried out, and/or

ad) when R_{13} is amino, treatment with an electrophilic aminating agent, as described, for example, in WO 96/36614, is carried out, and/or

ae) when R_1 and/or R_{11} are chlorine, bromine or iodine, treatment with a corresponding halogenating reagent is carried out.

Those synthesis sequences are illustrated in Reaction Scheme 10.

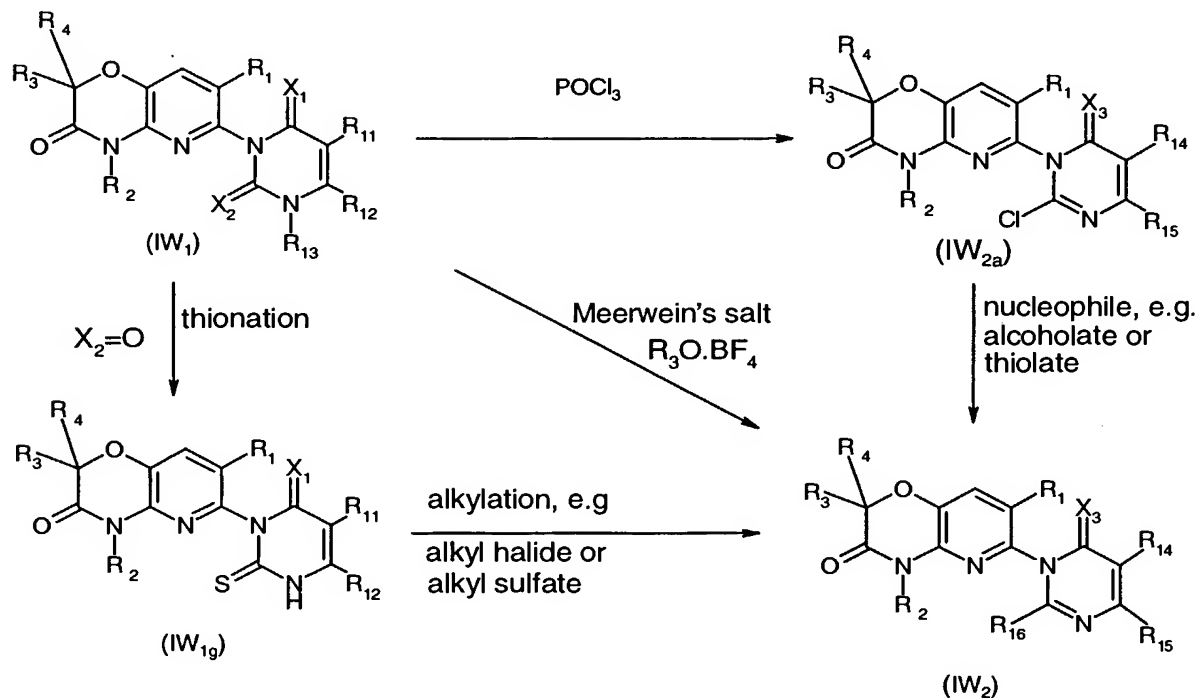
Reaction Scheme 10:



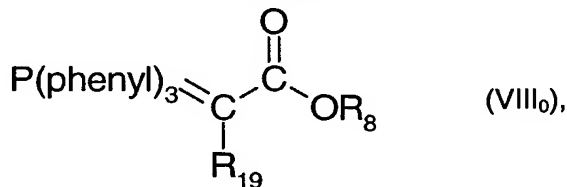
Compounds of formula I wherein W is a group W₂ can be obtained under particular conversion conditions from compounds of formula IW₁ wherein R₁₃ is hydrogen and X₂ is

oxygen or sulfur, either using an alkylating reagent or using a chlorinating reagent and a subsequent substitution reaction. Reaction Scheme 2₀ illustrates that process.

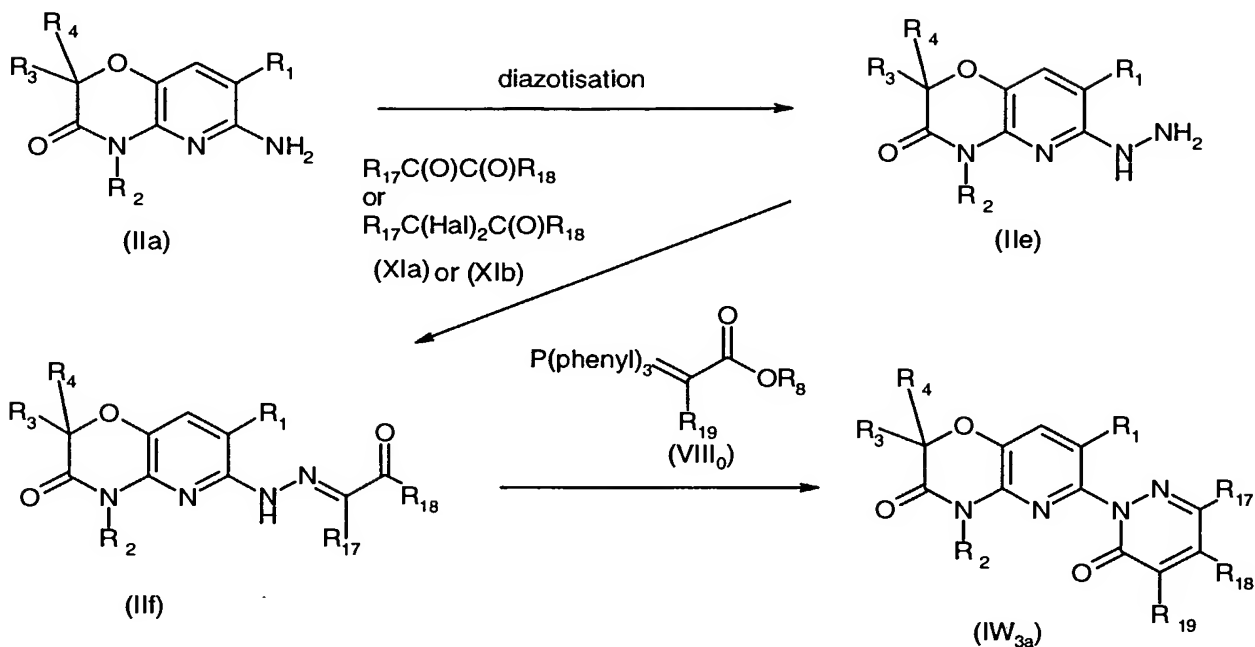
Reaction Scheme 2₀:



The process according to the invention described under variant b) for the preparation of compounds of formula I wherein W is a group W₃ is likewise carried out analogously to known processes and comprises first of all converting a compound of formula IIa, under diazotisation and condensation conditions, *via* a hydrazine derivative of formula IIe into a hydrazone of formula II_f, wherein R_{17} and R_{18} are as defined for formula I, and then condensing that hydrazone with a Wittig reagent of formula VIII₀



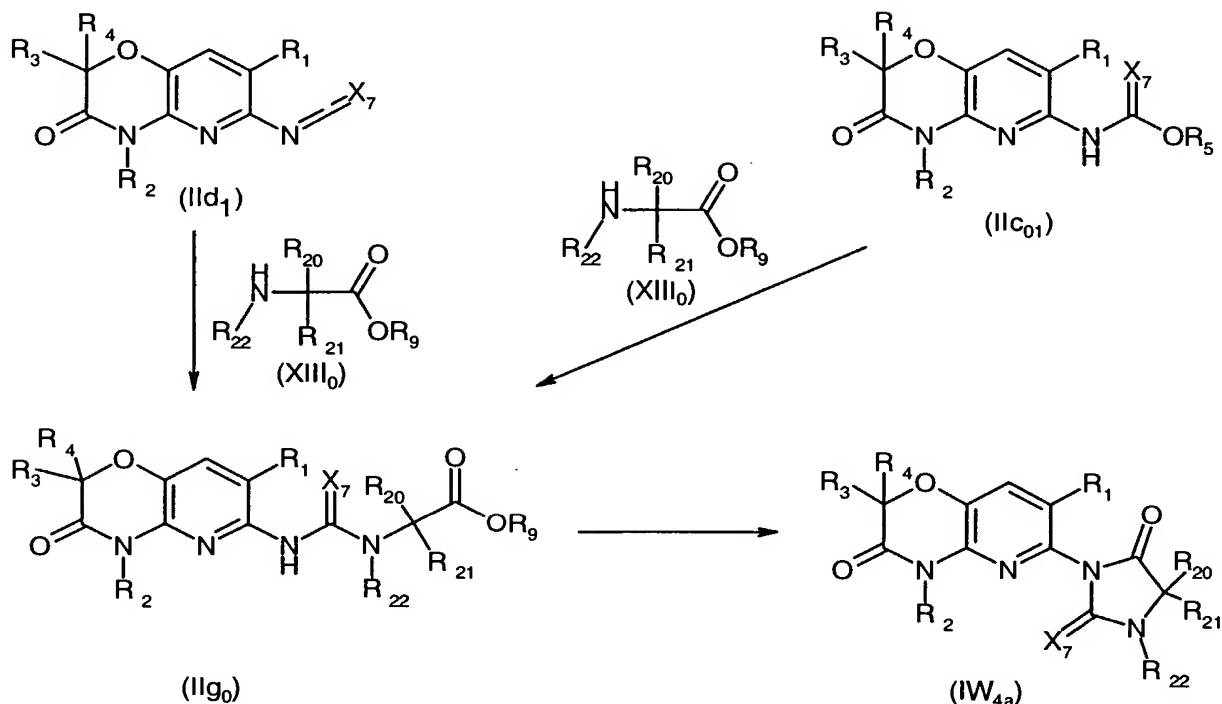
wherein R_{19} is as defined for formula I and R_8 is $\text{C}_1\text{-C}_4$ alkyl, in the presence of from 0.1 to 1.5 equivalents of a suitable base in an inert solvent to form the cyclic group W₃, and then, optionally, further reacting in an additional conversion reaction according to the corresponding meanings of R_1 , R_2 , R_{18} and X_5 in analogous manner to that described under aa), ac) or ae). Reaction Scheme 3₀ illustrates that reaction sequence.

Reaction Scheme 3₀:

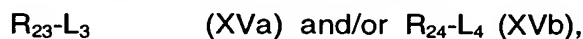
The process according to the invention described under variant b) for the preparation of compounds of formula I wherein W is a group W₄ is likewise carried out analogously to known processes, as described, for example, in EP-A-0 272 594, EP-A-0 493 323, DE-A-3 643 748, WO 95/23509, US-A-5 665 681 and US-A-5 661 109, and comprises reacting a compound of formula IIc₀₁ or IId₁ with an amino acid ester of formula XIII₀, wherein R₂₀, R₂₁ and R₂₂ are as defined for formula I and R₉ is C₁-C₄alkyl, and condensing the resulting intermediate of formula IIg₀ to form the cyclic group of formula W_{4a} and then, optionally, further reacting the resulting compound in an additional conversion reaction according to the corresponding meanings of R₁, R₂, R₂₀, R₂₁ and X₇ as described under aa), ac) or ae) or, when R₂₂ is hydrogen, further reacting the resulting compound with an appropriate alkylating agent of formula X



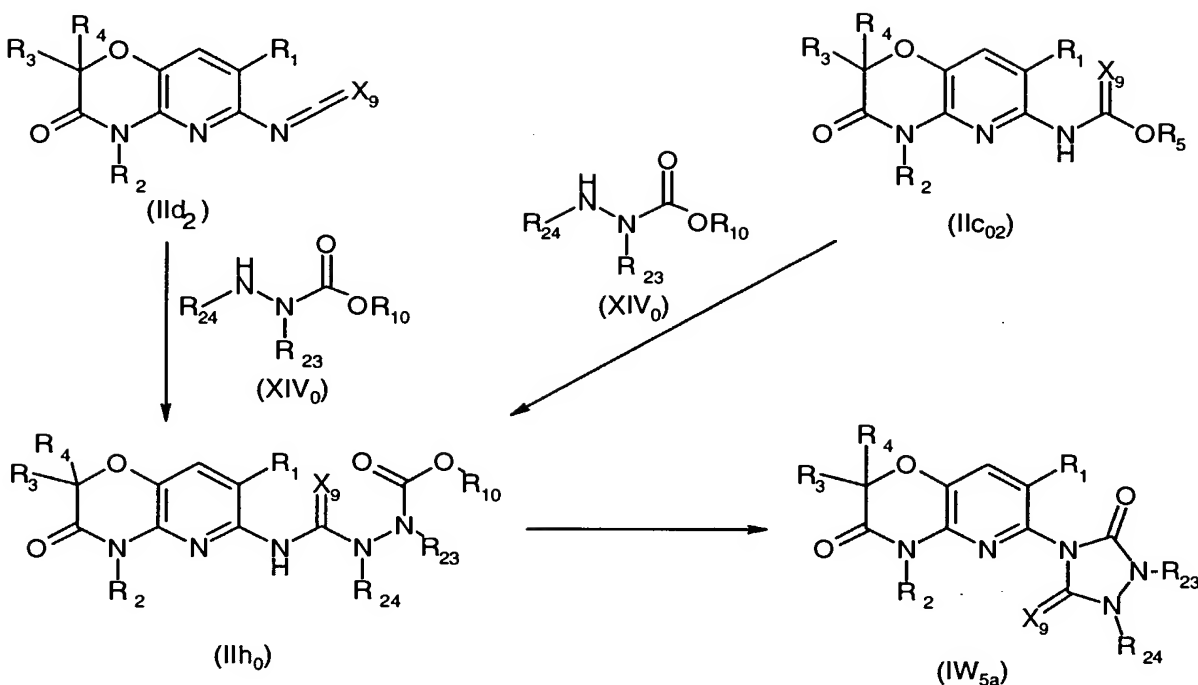
wherein R₂₂ is C₁-C₃alkyl and L₅ is a leaving group, for example halogen, especially chlorine, bromine or iodine, in the presence of a base. Reaction Scheme 4₀ illustrates that reaction sequence.

Reaction Scheme 4₀:

The process according to the invention described under variant b) for the preparation of compounds of formula I wherein W is a group W₅ is carried out analogously to known processes, as described, for example, in EP-A-0 210 137, DE-A-2 526 358, EP-A-0 075 267 and EP-A-0 370 955, and comprises reacting a compound of formula IIc₀₂ or IId₂ with a hydrazide ester of formula XIV₀, wherein R₂₃ and R₂₄ are as defined for formula I and R₁₀ is C₁-C₄alkyl, in the presence of a base and a suitable solvent, and then condensing the intermediate of formula IIh₀ to form the cyclic group of formula W_{5a} and then, optionally, further reacting the resulting compound in an additional conversion reaction according to the corresponding meanings of R₁, R₂, R₂₃, R₂₄ and X₉ in analogous manner to that described under aa), ac) or ae) or, when R₂₃ and/or R₂₄ are hydrogen, further reacting the resulting compound with an appropriate alkylating agent of formula XVa and/or XVb



wherein R₂₃ and R₂₄ are as defined for formula I with the exception of R₂₃ and R₂₄ as hydrogen, and L₃ and L₄ are leaving groups, for example halogen, especially chlorine, bromine or iodine, in the presence of a base. Reaction Scheme 5₀ illustrates that reaction sequence.

Reaction Scheme 5₀:

In analogous manner, compounds of formula I wherein W is a group W₆, W₇, W₈, W₉ or W₁₀ can also be prepared in accordance with the processes according to the invention described under variant b).

In process variant c), suitable catalysts are especially metal catalysts, for example Pd(PPh₃)₄, Pd(PPh₃)Cl₂, Pd(OAc)₂ and copper iodide. Further suitable catalytic additives include various phosphine ligands, for example biphenyl-2-bis-tert-butylphosphine, and various bases, for example triethylamine, potassium carbonate and caesium fluoride.

The process according to the invention described under variant d) for the preparation of compounds of formula I wherein W is, for example, a group W₁₀₀, R₁₀₁ is difluoromethoxy, R₁₀₂ is hydrogen, chlorine or bromine and R₁, R₂, R₃, R₄ and R₁₀₀ are as defined for formula I, is likewise carried out analogously to known synthesis processes, as described, for example, in EP-A-0 839 808 and WO 98/21199, and comprises converting a carboxylic acid of formula IIu₁, via its acid chloride of formula IIu₂, using a suitable malonic acid ester of formula XL₀

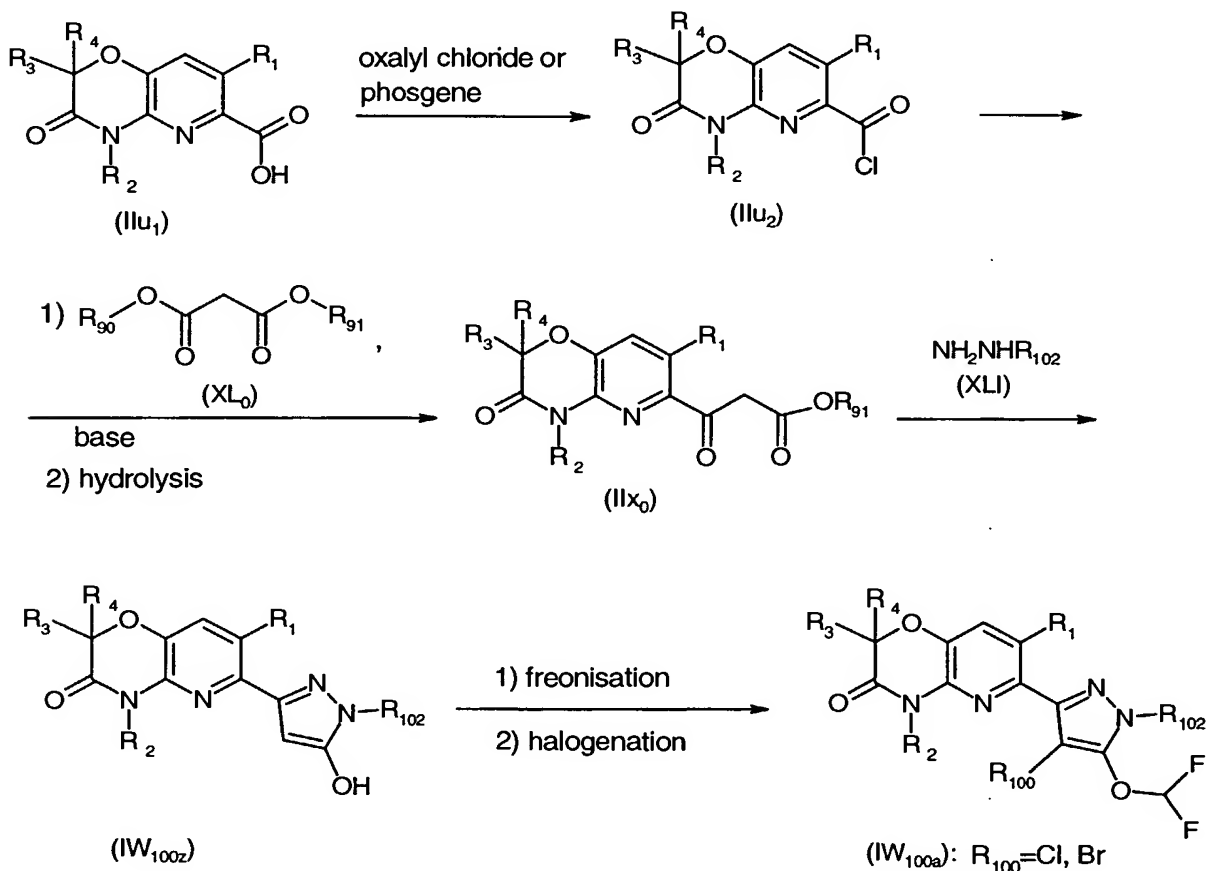


wherein R_{90} is hydrogen, trimethylsilyl or C_1 - C_4 alkyl and R_{91} is C_1 - C_4 alkyl, in the presence of a suitable base and an inert solvent, into the keto ester of formula IIx_0 , and then cyclising that keto ester with a corresponding hydrazine derivative of formula XLI



wherein R_{102} is as defined for formula I, to form a pyrazolone derivative of formula IW_{100z} , which is then subjected to freonisation and subsequently to a halogenation reaction. In the first stage therein, instead of R_{90} as hydrogen, a sodium, potassium or magnesium salt of the malonic acid monoalkyl ester may also be advantageously used. The freonisation is advantageously performed in the presence of a suitable base in water or in a two-phase system consisting of a chlorinated hydrocarbon and water or, optionally, advantageously in a closed system and under slight overpressure. Reaction Scheme 11₀ illustrates that reaction sequence for the preparation of compounds of formula IW_{100a} .

Reaction Scheme 11₀:



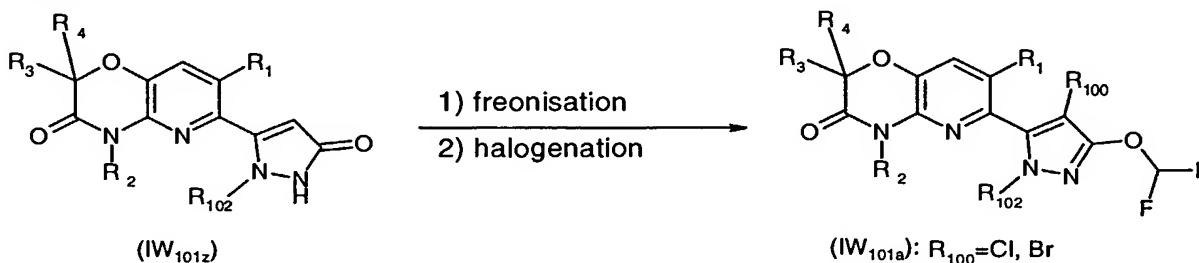
In further conversion reactions, in analogous manner to that described under ac) above, the compounds of formula IW_{100a} wherein R_1 and/or R_2 are hydrogen may be further reacted,

according to process variant a), with an appropriate alkylating reagent of formula IV R_2-L_2 (IV) or, as described under ae), with a corresponding halogenating reagent. If the halogenation reaction is performed in the presence of an excess of halogenating reagent, there are formed, from compounds of formula IW_{100z} wherein R_1 is hydrogen, compounds of formula IW_{100a} wherein both R_1 and R_{100} are accordingly simultaneously chlorine or bromine. When unsubstituted hydrazine of formula XLI wherein R_{102} is hydrogen is used, compounds of formula IW_{100z} are obtained wherein R_{102} is hydrogen. Those compounds can be reacted with an appropriate alkylating agent of formula XVI

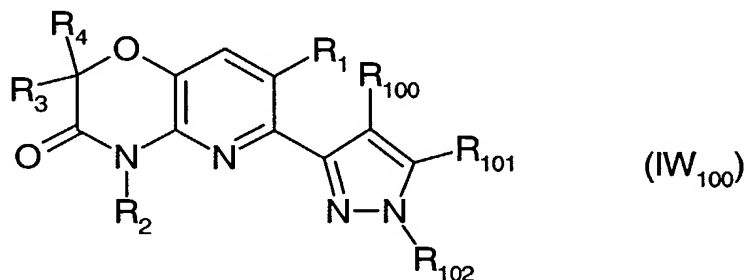


wherein R_{102} is as defined for formula I with the exception of R_{102} as hydrogen, and L_{10} is a leaving group, to form the corresponding compound of formula IW_{100a} wherein R_{102} is as defined. In addition, in that alkylation reaction there are also formed the isomeric compounds of formula IW_{101z} , which, after the freonisation reaction and, optionally, the halogenation reaction, form the corresponding isomeric compounds of formula IW_{101a} , as illustrated in Reaction Scheme 12₀.

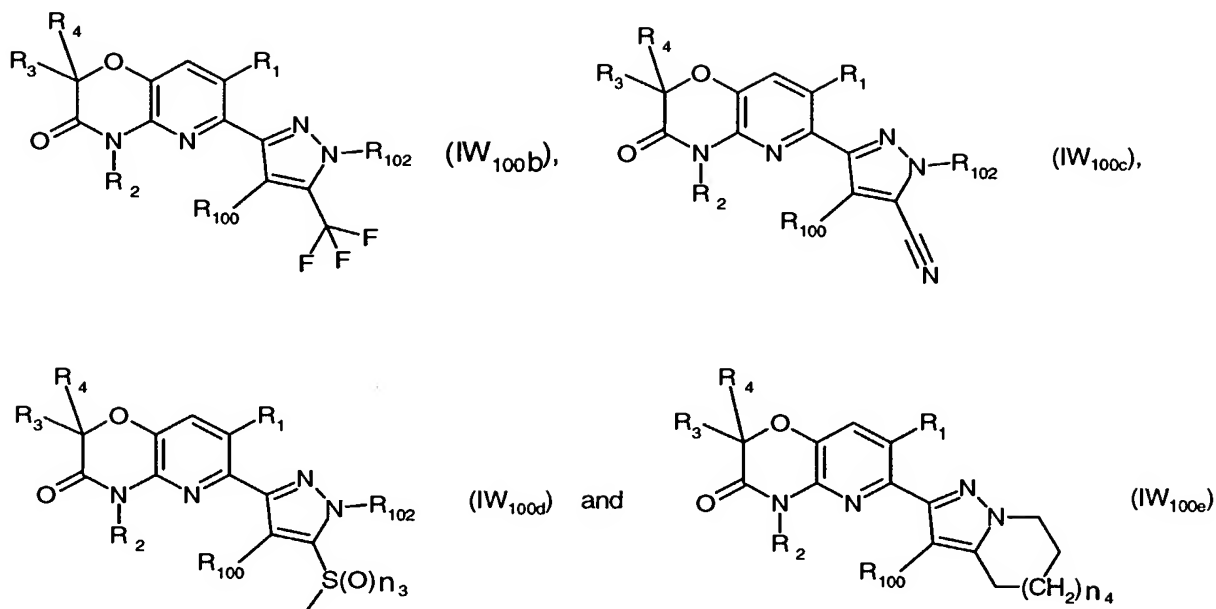
Reaction Scheme 12₀:



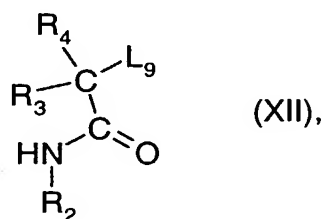
Corresponding synthesis processes for the preparation of compounds of formula IW_{100}



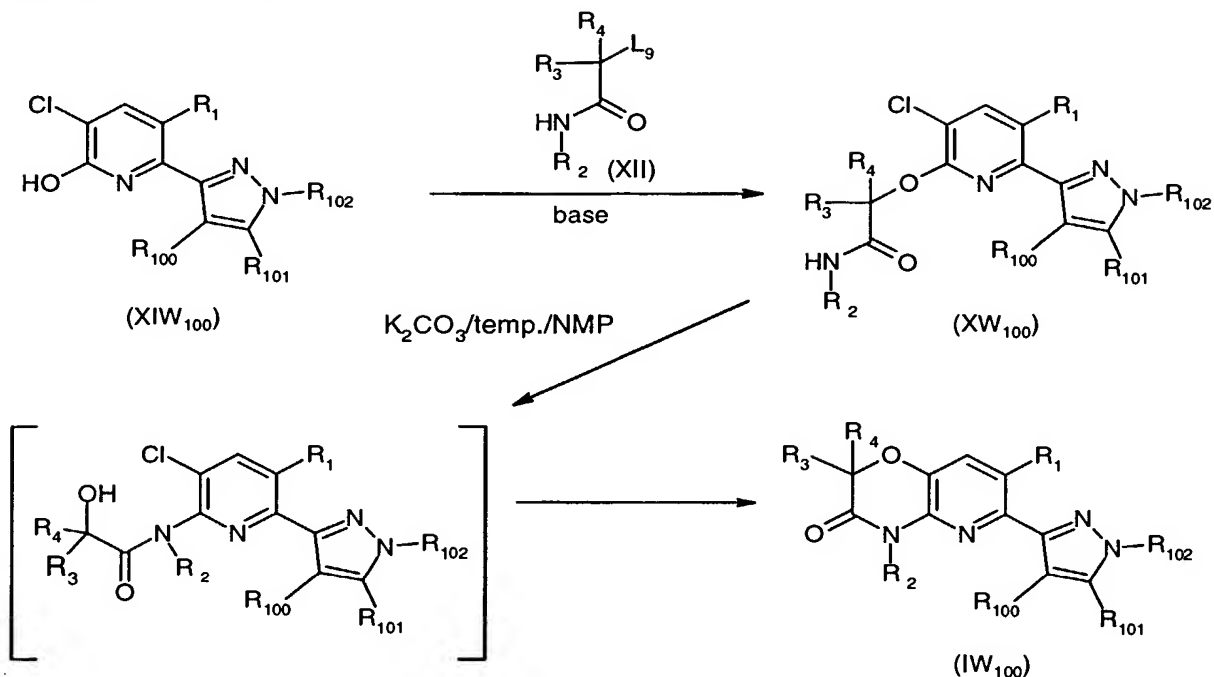
wherein R_{101} is trifluoromethyl (compounds of formula IW_{100b}), cyano (compounds of formula IW_{100c}), methylthio ($n_3=0$), methylsulfinyl ($n_3=1$) or methylsulfonyl ($n_3=2$) (compounds of formula IW_{100d}), or wherein R_{101} and R_{102} together form a C₃-C₅alkylene chain ($n_4 = 0, 1$ or 2) (compounds of formula IW_{100e}) are known, for example, from WO 98/21199 and EP-A-0 839 808.



Compounds of formula IW₁₀₀ may also be prepared according to process variant f) described above by reacting a compound of formula XIW₁₀₀, wherein R₁ and W are as defined for formula I, with a corresponding acetamide of formula XII



wherein R₂, R₃ and R₄ are as defined for formula I and L₉ is a leaving group, for example chlorine, bromine, mesyloxy, tosyloxy or trifluoromethylsulfonyloxy, in the presence of a base and an inert solvent, for example N-methylpyrrolidone (NMP), at temperatures of from 20° to 250°C and at normal pressure or under slight overpressure, but preferably at the boiling point of the solvent in question. Reaction Scheme 22₀ illustrates that reaction sequence.

Reaction Scheme 22₀:

Compounds of formulae **XW₁₀₀** and **XIW₁₀₀** either are known or can be prepared analogously to the processes described in WO 98/42698.

Compounds of formula I wherein W is a group **W₁₀₃** (compounds of formula **IW₁₀₃**) can be prepared in analogous manner to that described in WO 99/06394 and WO 98/07720.

Compounds of formula I wherein W is a group **W₁₀₄** (compounds of formula **IW₁₀₄**) can be prepared in analogous manner to that described in WO 97/11060.

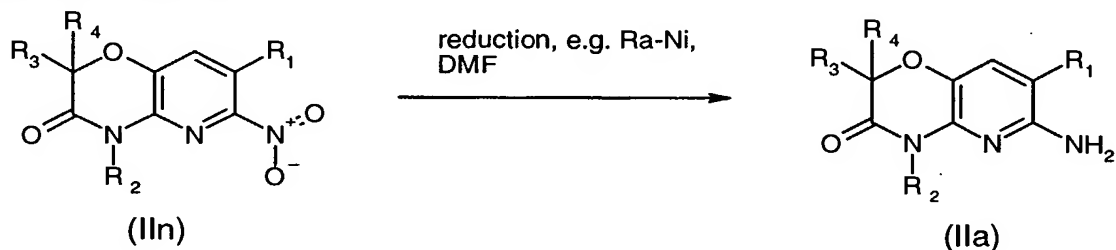
Compounds of formula I wherein W is a group **W₁₀₇** (compounds of formula **IW₁₀₇**), can be prepared in analogous manner to that described in WO 97/06150.

The resulting compounds of formula I and salts thereof can be isolated in customary manner by concentrating or evaporating off the solvent and can be purified by recrystallisation or trituration of the solid residue in solvents in which they are not readily soluble, for example ethers or aromatic or chlorinated hydrocarbons. Moreover, the person skilled in the art will be familiar with the sequence in which certain reactions among the process variants described should be advantageously performed in order to avoid possible undesired competing reactions.

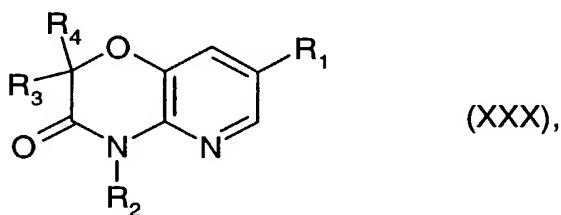
Where synthesis is not directed at the isolation of pure isomers, the product may be in the form of a mixture of two or more isomers. The isomers can be separated according to methods known *per se*. If desired, pure optically active isomers can, for example, also be prepared by synthesis starting from corresponding optically active starting materials.

The 6-amino-4H-pyrido[3,2-b][1,4]oxazin-3-ones of formula IIa (Reaction Scheme 1b) used as starting compounds can be prepared by reducing 6-nitro-4H-pyrido[3,2-b][1,4]oxazin-3-one of formula IIIn, wherein R₁, R₂, R₃ and R₄ are as defined for formula I, under known reaction conditions, for example using iron trichloride (Fe(III)Cl₃) in acetic acid according to Béchamps or in the presence of hydrogen and a metal catalyst, for example Raney nickel or palladium on activated carbon, in an inert diluent, for example an ether, especially tetrahydrofuran or dioxane, an alcohol, especially ethanol, an amide, especially N,N-dimethylformamide (DMF) or N-methylpyrrolidone (NMP) or water, as illustrated in Reaction Scheme 13.

Reaction Scheme 13:



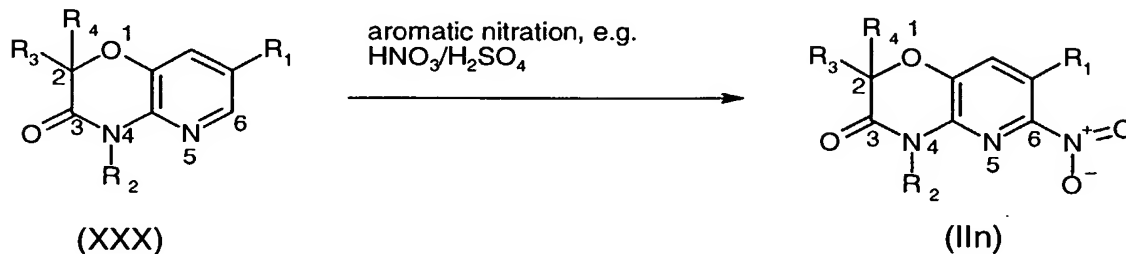
The 6-nitro-4H-pyrido[3,2-b][1,4]oxazin-3-ones of formula IIIn used as starting compounds in Reaction Scheme 13 can be obtained selectively by means of aromatic nitration of compounds of formula XXX



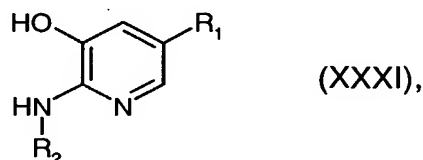
wherein R₁ to R₄ are as defined for formula I, under standard conditions, for example using HNO₃/H₂SO₄, as illustrated in Reaction Scheme 14, and then further functionalised according to the definitions of R₁ and R₂ for formula I in accordance with standard processes, for example alkylation and halogenation as described under ac) and ae). The aromatic nitration proceeds selectively in the 6-position of the 4-H-pyrido[1,4]oxazinone ring independently of the substituent R₁ (cf., in that respect, the analogous halogenation

reaction, which, in contrast, takes place predominantly in the 7-position, e.g. US-A-3 854 926 and WO 88/08705).

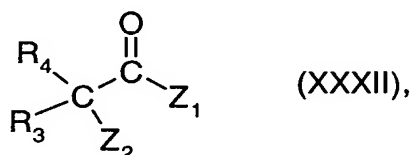
Reaction Scheme 14



The 4H-pyrido[3,2-b][1,4]oxazin-3-ones of formula XXX used as starting compounds in Reaction Scheme 14 can be obtained analogously to known processes, as described, for example, in *Acta Chimica Scandinavica* 23, 2322 (1969), from 2-amino-3-hydroxy-pyridine derivatives of formula XXXI



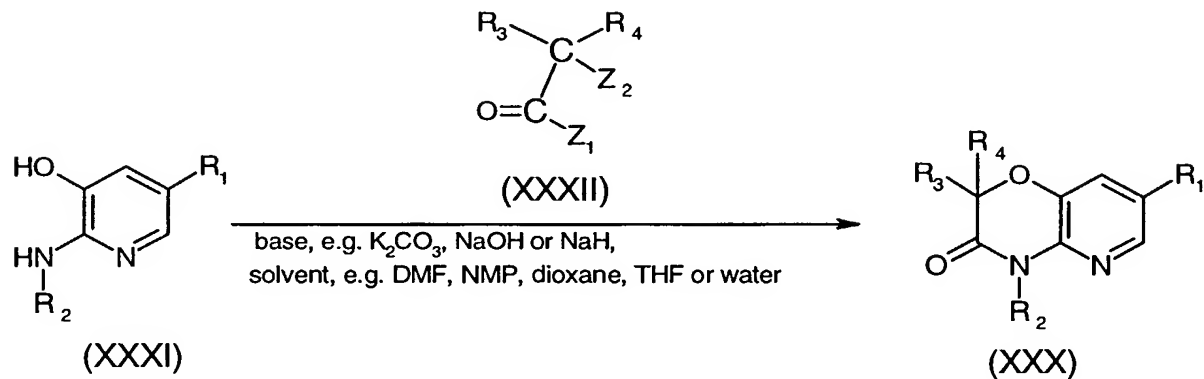
wherein R_1 and R_2 are as defined for formula I, by reacting such a compound with a compound of formula XXXII



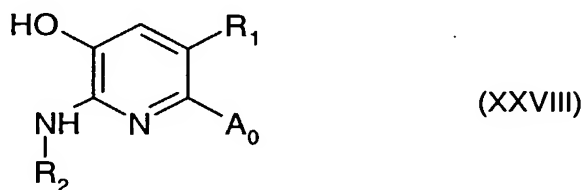
wherein R_3 and R_4 are as defined for formula I, Z_1 is a C_1 - C_4 alkoxy group, especially methoxy or ethoxy, or halogen, especially chlorine or bromine, and Z_2 is a leaving group, for example halogen, especially chlorine or bromine, or sulfonate, especially methylsulfonyloxy or phenylsulfonyloxy, in the presence of a suitable base, for example a carbonate, e.g. sodium or potassium carbonate, an alkali metal hydroxide, e.g. sodium or potassium hydroxide, or an alkali or alkaline earth metal hydride, e.g. sodium hydride, and in the presence of a suitable solvent, for example an ether, e.g. tetrahydrofuran or dioxane, an amide, e.g. DMF or NMP, or water, or a mixture of those solvents, as illustrated in Reaction Scheme 15. The compounds of formula XXX thereby obtained may then be further functionalised according to the definitions of R_1 and R_2 for formula I as described above, for

example, under ac) (alkylation using R_2-L_2 (IV)) and/or ae) (halogenation) and/or af) (fluorination).

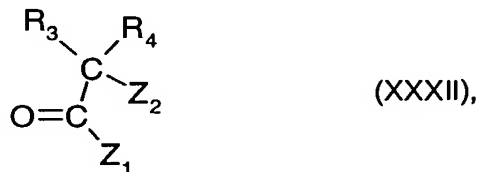
Reaction Scheme 15:



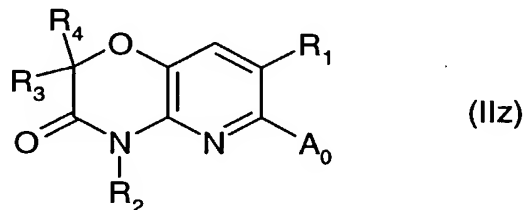
In analogous manner, for example, according to process variant g) and Reaction Scheme 15a, starting from a compound of formula XXVIII



and a compound of formula XXXII



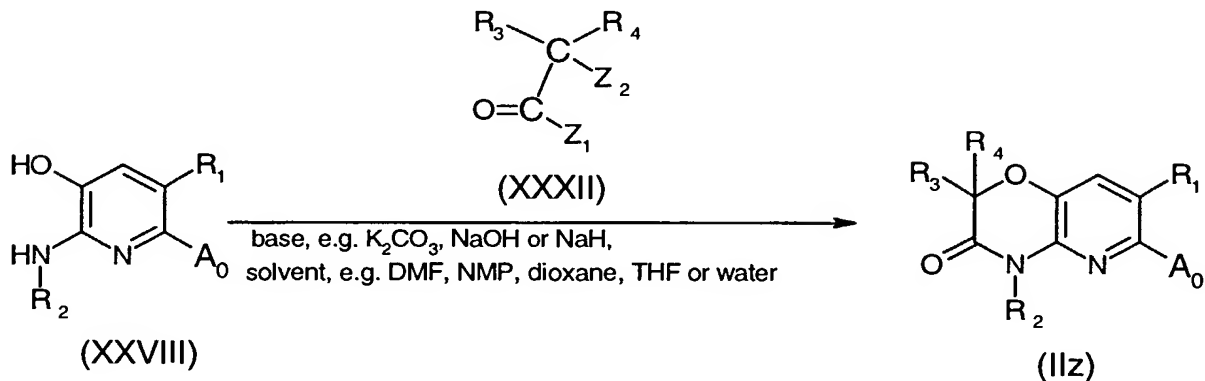
it is also possible to prepare compounds of formula IIz



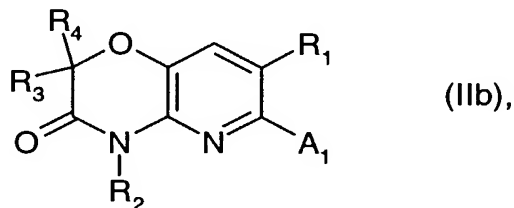
wherein in the compounds of formulae XXVIII, XXXII and IIz the substituents R_1 , R_2 , R_3 and R_4 are as defined for formula I, Z_1 is a C_1 - C_4 alkoxy group, especially methoxy or ethoxy, or halogen, especially chlorine or bromine, Z_2 is a leaving group, for example halogen, especially chlorine or bromine, or sulfonate, especially methylsulfonyloxy or

phenylsulfonyloxy, and A_0 is chlorine or bromine (= compounds of formula IIb) or, especially, methyl or carboxy (= compounds of formula IIu).

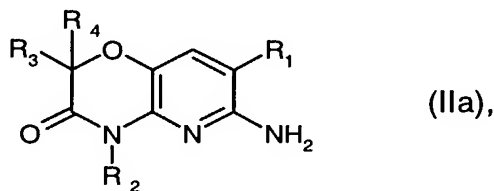
Reaction Scheme 15a:



The starting compounds of formula IIb



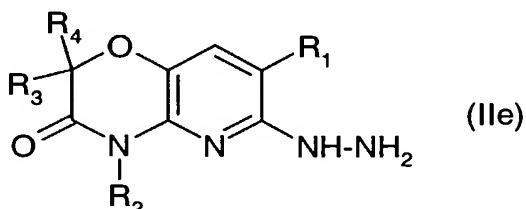
wherein R₁ to R₄ are as defined for formula I and A₁ is halogen, C₁-C₄alkylthio, C₁-C₄alkylsulfonyl, C₁-C₄alkylsulfonyloxy, hydroxy or trifluoromethylsulfonyloxy, used for process variant c) above can be prepared, for example, from compounds of formula IIa



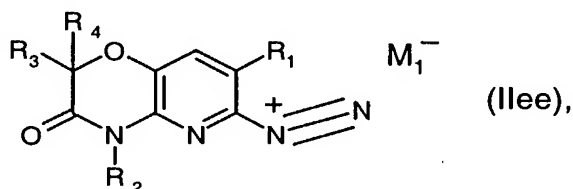
wherein R₁ to R₄ are as defined, by means of standard processes, for example diazotisation and boiling of the resulting diazonium salt (compound of formula IIee in Reaction Scheme 16b) to form the compound of formula IIb wherein A₁ is hydroxy, or by a Sandmeyer reaction of the resulting diazonium salt, for example using copper(I) chloride or copper(I) bromide, to form the compounds of formula IIb wherein A₁ is halogen, especially chlorine or bromine, and subsequently subjecting the hydroxy compound to treatment with C₁-C₄alkylsulfonic acid anhydride or trifluoromethanesulfonic acid anhydride to yield the compounds of formula IIb wherein A₁ is C₁-C₄alkylsulfonyloxy or trifluoromethylsulfonyloxy, or subsequently substituting the halogen compound of formula IIb (A = halogen) with C₁-C₄alkylthiolates to yield the compounds of formula IIb wherein A₁ is C₁-C₄alkylthio and then

optionally converting those compounds by means of oxidation, for example using m-chloroperbenzoic acid or hydrogen peroxide in acetic acid, into the corresponding compounds of formula IIb wherein A_1 is C_1 - C_4 alkylsulfonyl.

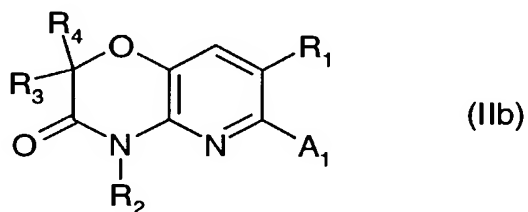
The hydrazine derivatives of formula IIe



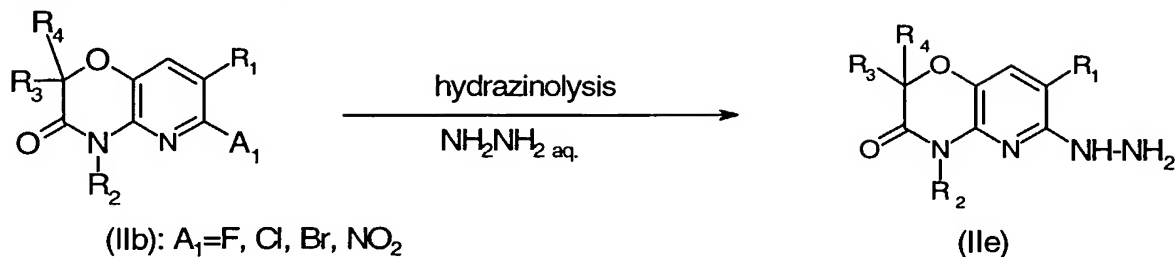
used in Reaction Schemes 3, 6, 6a and 10 can be obtained either by means of diazotisation of compounds of formula IIa, for example using sodium nitrite in hydrochloric acid or sulfuric acid, and reduction, for example using sodium sulfite or tin(II) chloride (SnCl_2), of the resulting diazonium salts of formula IIee



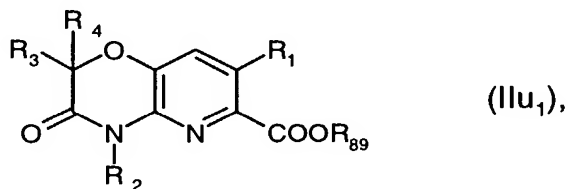
the substituents R_1 to R_4 in the compounds of formulae IIe and IIee being as defined for formula I, and M_1^- is an anion for example hydrogen sulfate or tetrafluoroborate, or halide, for example chloride, or by means of hydrazinolysis of the compounds of formula IIb



wherein R_1 to R_4 are as defined and A_1 is fluorine, chlorine, bromine or nitro, using hydrazine in water, ethanol or NMP, or in a mixture of those solvents, at temperatures of from 10° to 100°C , according to Reaction Scheme 15b.

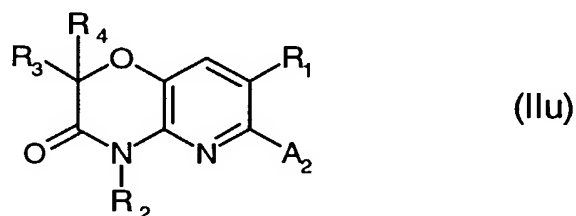
Reaction Scheme 15b:

The starting compounds used for process variant d) above, 3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazine-6-carboxylic acids or esters thereof of formula IIu₁



wherein R_1 to R_4 are as defined for formula I and R_{89} is hydrogen or C_1 - C_4 alkyl, can be prepared either

ba) by means of oxidation, using potassium permanganate, nitric acid or oxygen in the presence of a suitable metal catalyst, for example V_2O_5 , Na_2WO_4 , $Co(OAc)_3$ or $K_2Cr_2O_3$, starting from compounds of formula IIu



wherein R_1 to R_4 are as defined and A_2 is methyl (Reaction Scheme 16a), or

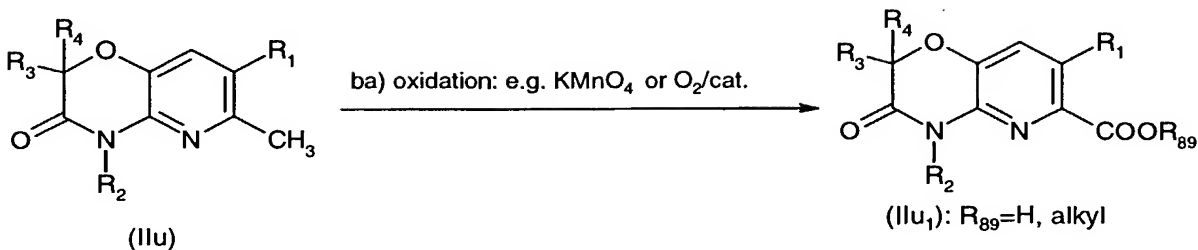
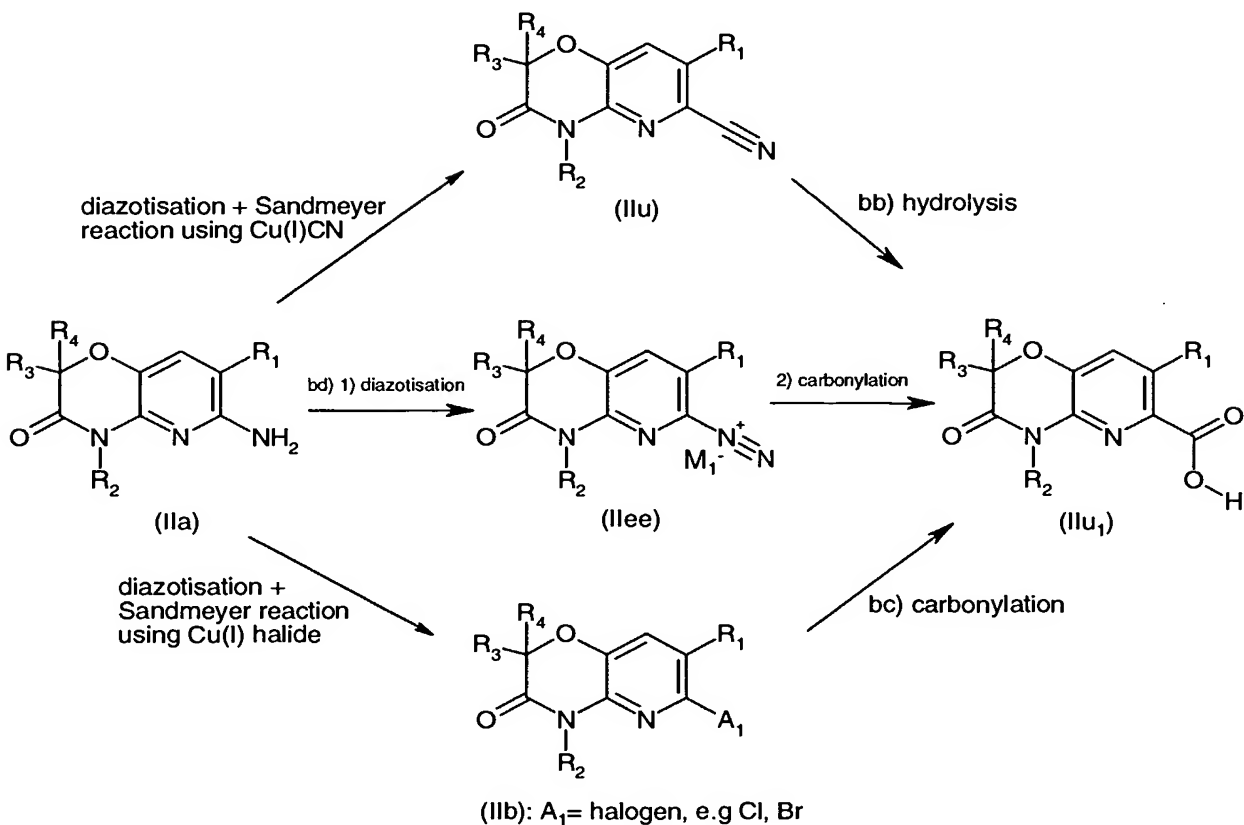
bb) by means of hydrolysis of compounds of formula IIu wherein R_1 to R_4 are as defined and A_2 is cyano, or

bc) by means of carbonylation of compounds of formula IIb wherein R_1 to R_4 are as defined and A_1 is chlorine or bromine, or

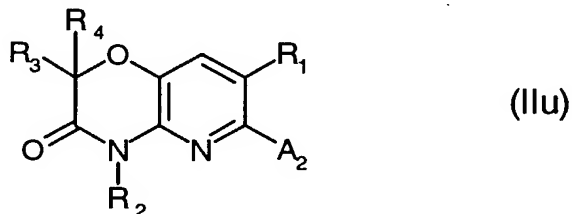
bd) by means of 1) diazotisation of the amines of formula IIa and 2) subsequent carbonylation of the diazonium salts of formula IIee obtained.

The cyano compounds of formula IIu used in process bb) can be obtained by means of diazotisation and a Sandmeyer reaction with addition of copper cyanide ($Cu(I)CN$).

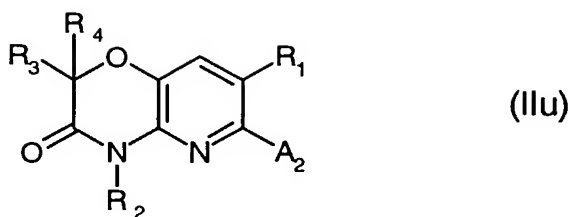
Reaction Schemes 16a and 16b illustrate those conversions in diagrammatic form.

Reaction Scheme 16a:Reaction Scheme 16b:

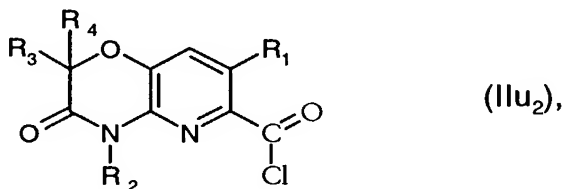
The starting compounds of formula IIu



wherein R₁, R₂, R₃ and R₄ are as defined for formula I and A₂ is formyl or acyl, used in process variant d) can, for example, be prepared by standard methods, starting from compounds of formula IIu

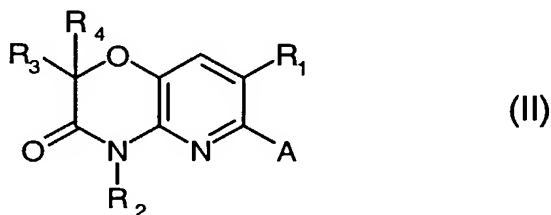


wherein R_1 to R_4 are as defined and A_2 is cyano, by means of reduction of the cyano group, for example using dibutylaluminium hydride (DIBAH), or starting from compounds of formula IIu₂

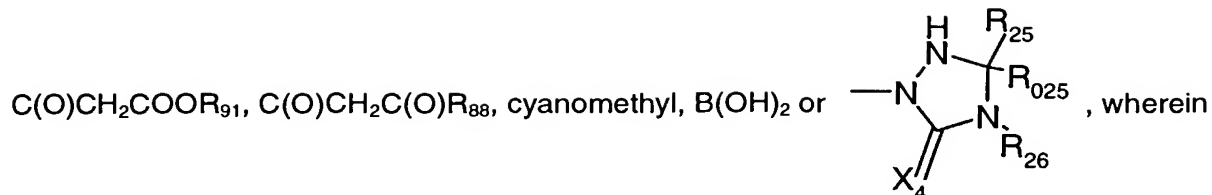


wherein R_1 to R_4 are as defined, by means of a Grignard reaction using methylmagnesium chloride, or using the reagent O,N-dimethyl acetamide.

The compounds of formula II



wherein R_1 to R_4 are as defined for formula I and A is fluorine, C₁-C₄alkylthio, C₁-C₄alkylsulfonyl, phenylthio, phenylsulfonyl, C₁-C₄alkylsulfonyloxy, trifluoromethylsulfonyloxy, hydroxy, nitro, amino, isocyanato, isothiocyanato, hydrazino, a group NHC(X₂)X₀R₅, NHC(X₇)X₀R₅, NHC(X₈)X₀R₅, NHC(X₉)X₀R₅, NHC(X₃)R₁₆, NHN=C(R₁₇)C(O)R₁₈, NHC(X₇)N(R₂₂)C(R₂₀)R₂₁C(X₆)OR₉, NHC(X₉)NR₂₄NR₂₃C(X₈)OR₁₀, NHC(X₈)NR₂₃NHR₂₄, NHN=C(R₂₅)COOH, NHN=C(R₂₅)R₀₂₅, N(C(X₄)-NHR₂₆)N=CR₂₅R₀₂₅, N(C(X₄)-NHR₂₆)NH₂, NHN=C(R₂₅)N(R₂₆)C(X₄)OR₈₄, N(C(X₄)-NHR₂₆)NHC(O)OR₈₄, N(C(X₁₉)-NHR₅₀)NHC(O)OR₈₄, NHC(X₁₂)NHR₂₆, NHC(O)C(R₂₈)=C(R₂₇)C(O)OR₈₅, NHC(=NR₃₉)NHR₃₈, NHC(Y₂)NR₄₀NHR₄₁, NHC(Y₂)NR₄₀NR₄₁C(O)OR₉, NHN=C(R₄₂)C(O)NHR₄₃, NHN=C(R₄₂)C(O)N(R₄₃)C(O)OR₈₅, N(R₄₃)COOR₈₅, NHC(R₅₃)=NNHC(X₂₁)OR₈₅, NHC(S)NHC(=NR₅₇)R₅₆, NHC(X₂₃)NHR₅₈C(X₂₅)NHR₅₉, N(C(X₂₄)-NHR₅₉)C(X₂₃)X₀R₅, ethyl, vinyl, ethynyl, C≡CC(O)OR₈₆, C≡CC(O)R₈₇, acyl, formyl, cyano, carboxy, C(O)OR₈₉, C(O)C(O)OR₉₀,



R_{16} , R_{17} , R_{18} , R_{20} , R_{21} , R_{22} , R_{23} , R_{24} , R_{25} , R_{26} , R_{27} , R_{28} , R_{38} , R_{39} , R_{40} , R_{41} , R_{42} , R_{43} , R_{50} , R_{53} , R_{56} and R_{57} are as defined in claim 1; R_5 , R_9 , R_{025} , R_{84} , R_{86} , R_{89} , R_{90} and R_{91} are each independently of the others C_1 - C_4 alkyl or phenyl; R_{10} and R_{85} are hydrogen or C_1 - C_4 alkyl; R_{87} and R_{88} are C_1 - C_4 alkyl, formyl, $\text{CH}(\text{C}_1\text{-C}_4\text{alkoxy})$ or C_1 - C_4 haloalkyl; X_2 , X_3 , X_4 , X_6 , X_7 , X_8 , X_9 , X_{12} , X_{19} , X_{21} and Y_2 are oxygen or sulfur; and X_0 is oxygen, sulfur or amino, are new, and the present invention also relates to those compounds. Of those compounds, preference is given to those wherein A is fluorine, C_1 - C_4 alkylthio, C_1 - C_4 alkylsulfonyloxy, trifluoromethylsulfonyloxy, hydroxy, nitro, amino, isocyanato, isothiocyanato, hydrazino, a group $\text{NHC}(\text{X}_2)\text{OR}_5$, $\text{NHC}(\text{X}_7)\text{OR}_5$, $\text{NHC}(\text{X}_8)\text{OR}_5$, $\text{NHC}(\text{X}_9)\text{OR}_5$, $\text{NHN}=\text{C}(\text{R}_{17})\text{C(O)R}_{18}$, $\text{NHC}(\text{X}_7)\text{N}(\text{R}_{22})\text{CR}_{20}\text{R}_{21}\text{C(O)OR}_9$, $\text{NHC}(\text{X}_9)\text{NR}_{24}\text{NR}_{23}\text{C(O)OR}_{10}$, ethyl, vinyl, ethynyl, $\text{C}\equiv\text{CC(O)OR}_{86}$, $\text{C}\equiv\text{CC(O)R}_{87}$, acyl, formyl, cyano, carboxy, C(O)OR_{89} , $\text{C(O)CH}_2\text{COOR}_{91}$, $\text{C(O)CH}_2\text{C(O)R}_{88}$, cyanomethyl or B(OH)_2 , wherein R_5 , R_9 , R_{10} , R_{86} , R_{89} and R_{91} are each independently of the others C_1 - C_4 alkyl; R_{17} , R_{18} , R_{20} , R_{21} , R_{22} , R_{23} and R_{24} are as defined for formula I; R_{87} and R_{88} are each independently of the other C_1 - C_4 alkyl, formyl, $\text{CH}(\text{C}_1\text{-C}_4\text{alkoxy})$ or C_1 - C_4 haloalkyl; and X_2 , X_7 , X_8 and X_9 are oxygen or sulfur.

The compounds of formula II wherein A is methyl, chlorine or bromine (compounds of formulae IIa and IIb) are known from CH-A-452 528, CH-A-452 529 and US-A-3 854 926 or can be prepared analogously to the processes described therein or analogously to Reaction Scheme 15.

The compounds of formula II wherein A is hydrogen (compounds of formula XXX) are known, for example, from Acta Chimica Scandinavica 23, 2322 (1969), CH-A-452 528, US-A-3 854 926 and WO 88/08705 or can be prepared analogously to the processes described therein or analogously to Reaction Scheme 15.

The compounds of formula XXVIII wherein, for example, A_0 is methyl or carboxy are known from CH-A-452 528 and J. Heterocyclic Chem. 13, 1103 (1976) or can be prepared analogously to the processes described therein.

The compounds of formula XXXI are either known, for example, where R₁ is hydrogen, from *Acta Chimica Scandinavica*, 23, 1785 (1969) and, where R₁ is chlorine or bromine, from *Helv. Chim. Acta* 60, 2062 (1977), or can be prepared analogously to the processes described therein.

Compounds of formulae XW and XIW are either known or can be prepared analogously to the processes described in WO 98/42698, WO 99/52892 and WO 99/52893.

The other compounds of formulae III, IV, V, VI, VIa, VIb, VIc, VI₀, VII, VIIa, VIIb, VIII, VIII₀, IX, IXa, IXb, X, Xa, XIa, XIb, XIc, XId, XIe, XIe₁, XIf, XIg, XIh, Xli, Xli₁, Xli₂, Xln, XII, XIII, XIII₀, XIV, XIVa, XIV₀, XVa, XVb, XVI, XVII, XVIII, XXV, XXVIa, XXVIb, XXVIc, XXVId, XXXII, XXXIII, XXXIVa, XXXIVb, XXXV, XXXVa, XXXVb, XXXVI, XXXVIIa, XXXVIIb, XXXVIII, XXXVIIIa, XXXVIIIb, XXXVIIIc, XXXVIIIId, XXXVIIIId₁, XXXIX, XL and XLI are known or can be prepared analogously to the processes described in the literature.

For the use according to the invention of the compounds of formula I or of compositions comprising them, there come into consideration all methods of application customary in agriculture, for example pre-emergence application, post-emergence application and seed dressing, and also various methods and techniques, such as, for example, the controlled release of active ingredient. For that purpose, a solution of the active ingredient is applied to mineral granule carriers or polymerised granules (urea-formaldehyde) and dried. If desired, it is also possible to apply a coating (coated granules) which allows the active ingredient to be released in metered amounts over a specific period of time.

The compounds of formula I can be used as herbicides in unmodified form, that is to say as they are obtained in synthesis, but they are preferably formulated in customary manner, together with the adjuvants conventionally employed in formulation technology, for example into emulsifiable concentrates, directly sprayable or dilutable solutions, dilute emulsions, wettable powders, soluble powders, dusts, granules or microcapsules. Such formulations are described, for example, in WO 97/34485 on pages 9 to 13. As with the nature of the compositions, the methods of application, such as spraying, atomising, dusting, wetting, scattering or pouring, are chosen in accordance with the intended objectives and the prevailing circumstances.

The formulations, that is to say the compositions, preparations or mixtures comprising the compound of formula I or at least one compound of formula I and, generally, one or more

solid or liquid formulation adjuvants, are prepared in known manner, for example by homogeneously mixing and/or grinding the active ingredients with the formulation adjuvants, for example solvents or solid carriers. Furthermore, surface-active compounds (surfactants) may also be used in the preparation of the formulations. Examples of solvents and solid carriers are given, for example, in WO 97/34485 on page 6.

Depending on the nature of the compound of formula I being formulated, suitable surface-active compounds are non-ionic, cationic and/or anionic surfactants and mixtures of surfactants having good emulsifying, dispersing and wetting properties.

Examples of suitable anionic, non-ionic and cationic surfactants are listed, for example, in WO 97/34485 on pages 7 and 8.

Furthermore, the surfactants customarily employed in formulation technology, which are described, *inter alia*, in "Mc Cutcheon's Detergents and Emulsifiers Annual" MC Publishing Corp., Ridgewood New Jersey, 1981, Stache, H., "Tensid-Taschenbuch", Carl Hanser Verlag, Munich/Vienna, 1981 and M. and J. Ash, "Encyclopedia of Surfactants", Vol I-III, Chemical Publishing Co., New York, 1980-81, are also suitable for preparation of the herbicidal compositions according to the invention.

The herbicidal formulations generally comprise from 0.1 to 99 % by weight, especially from 0.1 to 95 % by weight, of herbicide, from 1 to 99.9 % by weight, especially from 5 to 99.8 % by weight, of a solid or liquid formulation adjuvant and from 0 to 25 % by weight, especially from 0.1 to 25 % by weight, of a surfactant. Whereas commercial products will preferably be formulated as concentrates, the end user will normally employ dilute formulations. The compositions may also comprise further ingredients such as stabilisers, for example vegetable oils or epoxidised vegetable oils (epoxidised coconut oil, rapeseed oil or soybean oil), antifoams, for example silicone oil, preservatives, viscosity regulators, binders and tackifiers, as well as fertilisers or other active ingredients.

The compounds of formula I or a composition comprising that compound are generally applied to the plant or to the locus thereof at rates of application of from 0.001 to 4 kg/ha, especially from 0.005 to 2 kg/ha. The concentration required to achieve the desired effect can be determined by experiment. It is dependent on the nature of the action, the stage of development of the cultivated plant and of the weed and on the application (place, time, method) and may vary within wide limits as a function of those parameters.

The compounds of formula I are distinguished by herbicidal and growth-inhibiting properties, allowing them to be used in crops of useful plants, especially in cereals, cotton, soybeans, sugar beet, sugar cane, sorghum, plantation crops, rape, maize, sunflowers, vegetables, fodder plants and rice, and also for inhibiting plant growth and for non-selective weed control. Crops are to be understood as including also crops that have been made tolerant to herbicides or classes of herbicides as a result of conventional methods of breeding or genetic techniques. The weeds to be controlled may be either monocotyledonous or dicotyledonous weeds, for example *Stellaria*, *Nasturtium*, *Agrostis*, *Digitaria*, *Avena*, *Setaria*, *Sinapis*, *Lolium*, *Solanum*, *Echinochloa*, *Scirpus*, *Monochoria*, *Sagittaria*, *Bromus*, *Alopecurus*, *Sorghum halepense*, *Rottboellia*, *Cyperus*, *Abutilon*, *Sida*, *Xanthium*, *Amaranthus*, *Brachiaria*, *Euphorbia*, *Chenopodium*, *Ipomoea*, *Chrysanthemum*, *Galium*, *Viola* and *Veronica*.

The following Examples further illustrate but do not limit the invention.

Preparation Examples:

Example P1: 6-Nitro-4H-pyrido[3,2-b][1,4]oxazin-3-one

At 0-5°C, 150 g (1 mol) of 4H-pyrido[3,2-b][1,4]oxazin-3-one are introduced, in portions, into 400 ml of concentrated sulfuric acid. Then, while maintaining the temperature at below 10°C, 200 ml of fuming nitric acid are slowly added dropwise to the red solution and stirring is carried out for a further hour at 10-15°C. The reaction mixture is poured onto ice and the precipitated yellow product is filtered off and washed with cold water. Technical-grade 6-nitro-4H-pyrido[3,2-b][1,4]oxazin-3-one having a melting point of 247-252°C is thereby obtained which, after recrystallisation from methyl Cellosolve, melts at 254-256°C.

¹H-NMR ((CD₃)₂SO): 12.5 ppm (s, 1H); 8.00 ppm (d, J=8 Hz); 7.64 ppm (d, J=8.2 Hz); 4.88 ppm (s, 2H).

Example P2: 6-Amino-4H-pyrido[3,2-b][1,4]oxazin-3-one

156 g (0.8 mol) of the product obtained in Example P1 are dissolved in 2 litres of dimethylformamide and hydrogenated in the presence of 16 g of Raney nickel at 35-45°C until 53.8 litres of hydrogen have been absorbed. The mixture is then separated from the catalyst by filtration and diluted with water. Pure 6-amino-4H-pyrido[3,2-b][1,4]oxazin-3-one having a melting point of 279-281°C is thereby obtained. ¹H-NMR ((CD₃)₂SO): 10.78 ppm (s, NH); 7.03 ppm (d, 1H); 6.01 ppm (d, 1H); 6.29 ppm (s, 1H); 5.57 ppm (s, NH₂); 4.41 ppm (s, 2H).

Example P3: (3-Oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-carbamic acid ethyl ester

1.45 g (8.8 mmol) of 6-amino-4H-pyrido[3,2-b][1,4]oxazin-3-one are dissolved in 60 ml of pyridine and treated with 0.96 g (8.8 mmol) of chloroformic acid ethyl ester at 45°C. Stirring is then carried out for about 3 hours at that temperature, the precipitated pyridine hydrochloride is filtered off and the mixture is concentrated a little by evaporation. 150 ml of water are then added to the mixture, the pH is adjusted to 4 using concentrated hydrochloric acid and the precipitated crystals are filtered off. Virtually pure (3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-carbamic acid ethyl ester is thereby obtained. ¹H-NMR ((CD₃)₂SO): 11.08 ppm (s, NH); 9.78 ppm (s, NH); 7.33 ppm (m, 2H); 4.57 ppm (s, 2H); 4.12 ppm (q, 2H); 1.22 ppm (t, 3H).

Example P4: 3-(3-Oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione

1.5 g (6.3 mmol) of (3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-carbamic acid ethyl ester are introduced into a suspension of 0.36 g (15 mmol) of sodium hydride in N-methylpyrrolidone. Stirring is then carried out for about 30 minutes at 35°C, 1.3 g (7.3 mmol) of 3-amino-4,4,4-trifluoro-but-2-enoic acid ethyl ester are then added thereto, and the reaction mixture is heated at 100°C for 1.5 hours. Ice-water is added, the pH is adjusted to 2 using hydrochloric acid and the mixture is extracted several times with ethyl acetate. The combined organic phases are concentrated by evaporation to a volume of about 50 ml, whereupon 3-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione precipitates out as an almost pure product. ¹H-NMR ((CD₃)₂SO): 12.65 ppm (broad signal, NH); 11.40 ppm (s, NH); 7.52 ppm (d, 1H); 7.05 ppm (d, 1H); 6.36 ppm (s, 1H); 4.72 ppm (s, 2H).

Example P5: 1-Methyl-3-(4-methyl-3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione

0.33 g (1.0 mmol) of 3-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione is stirred with 0.31 g (2.0 mmol) of methyl iodide in the presence of 0.27 g (2.0 mmol) of potassium carbonate in 5 ml of acetonitrile at 20°C. After then being stirred for about 16 hours at 40-45°C, 30 ml of water are added and the mixture is acidified to pH 5 using hydrochloric acid and extracted with ethyl acetate. The product is purified by column chromatography (mobile phase: ethyl acetate/hexane 1/1). Pure 1-methyl-3-(4-methyl-3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione having a melting point of 211-211.5°C is obtained.

¹H-NMR (CDCl₃): 7.38 ppm (d, 1H); 6.90 ppm (d, 1H); 6.39 ppm (s, 1H); 4.74 ppm (s, 2H); 3.57 ppm (s, 3H); 3.41 ppm (s, 3H).

Example P6: 1-Methyl-3-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione

0.78 g (2.4 mmol) of 3-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione is stirred with 0.37 g (2.4 mmol) of methyl iodide in the presence of 0.25 g of potassium hydrogen carbonate in 5 ml of dimethylformamide at 20°C. After about 6 hours, 30 ml of water are added and the precipitated product is filtered off. Virtually pure 1-methyl-3-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione is obtained.

¹H-NMR ((CD₃)₂SO): 11.32 ppm (s, NH); 7.53 ppm (d, 1H); 7.01 ppm (d, 1H); 6.53 ppm (s, 1H); 4.74 ppm (s, 2H); 3.32 ppm (s, 3H).

Example P7: 1-Methyl-3-(3-oxo-4-prop-2-ynyl-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione

0.30 g (0.9 mmol) of 1-methyl-3-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione and 0.11 g (0.9 mmol) of propargyl bromide are heated in the presence of 0.14 g of potassium carbonate and a catalytic amount of 18-crown-6 in 10 ml of acetonitrile for 1 hour at reflux temperature. The solvent is evaporated off and the residue is filtered using a 1:1 mixture of ethyl acetate/hexane over a small amount of silica gel. The desired 1-methyl-3-(3-oxo-4-prop-2-ynyl-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione is obtained in the pure form having a melting point of 161.5-162°C.

Example P8: 3-(4-Isopropyl-3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-1-methyl-6-trifluoromethyl-1H-pyrimidine-2,4-dione

0.30 g (0.9 mmol) of 1-methyl-3-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione and 0.17 g (1.4 mmol) of isopropyl bromide are heated at 120°C in the presence of 0.19 g (1.4 mmol) of potassium carbonate and a catalytic amount of 18-crown-6 and a catalytic amount of potassium iodide in 2 ml of dimethylformamide in a pressure vessel for about 2 hours. The solvent is evaporated off under reduced pressure and the residue is chromatographed using a 1:2 mixture of ethyl acetate and hexane on silica gel. Pure 3-(4-isopropyl-3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-1-methyl-6-trifluoromethyl-1H-pyrimidine-2,4-dione is thereby obtained.

¹H-NMR (CDCl₃): 7.36 ppm (d, 1H); 6.87 ppm (d, 1H); 6.37 ppm (s, 1H); 5.16 ppm (m, 1H); 4.64 ppm (s, 2H); 3.57 ppm (s, 3H); 1.50 ppm (d, 6H).

Example P9: 6-(4-Chloro-5-difluoromethoxy-1-methyl-1H-pyrazol-3-yl)-7-fluoro-4H-pyrido[3,2-b][1,4]oxazin-3-one

0.5 g (1.3 mmol) of 2-(3-chloro-6-(4-chloro-5-difluoromethoxy-1-methyl-1H-pyrazol-3-yl)-5-fluoro-pyridin-2-yloxy)acetamide (WO 98/42698) is heated at 150°C in the presence of 0.18 g (1.3 mmol) of potassium carbonate in 10 ml of N-methylpyrrolidone (NMP) for 2 hours. The mixture is poured into water and extracted with diethyl ether. The residue that remains is chromatographed on silica gel. Pure 6-(4-chloro-5-difluoromethoxy-1-methyl-1H-pyrazol-3-yl)-7-fluoro-4H-pyrido[3,2-b][1,4]oxazin-3-one is thereby obtained as the more polar fraction.

¹H-NMR (CDCl₃): 8.40 ppm (s, NH); 7.18 ppm (d, 1H); 6.71 ppm (t, 1H); 4.74 ppm (s, 2H); 3.85 ppm (s, 3H).

Example P10: 3-Oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazine-6-carboxylic acid

3.66 g (84 mmol) of sodium hydride in the form of a 55 % dispersion in oil are introduced into 30 ml of dimethylformamide; then, 6.2 g of (40 mmol) of 2-amino-3-hydroxypyridin-6-yl-carboxylic acid (known from J. Heterocycl. Chem. 13, 1103 (1976)) are introduced, in portions, below 10°C and stirring is then carried out for 2 hours at 45°C until the evolution of hydrogen has ceased. 5.4 ml (44 mmol) of bromoacetic acid ethyl ester are then added dropwise. The suspension, which is difficult to stir, is further diluted with 15 ml of dimethylformamide and stirring is carried out for a further 2 hours at 70°C. The mixture is left to warm up to 20°C, water is added and extraction at pH 8 is carried out with diethyl ether. The aqueous phase is adjusted to pH 2.6 using hydrochloric acid and extracted with ethyl acetate. The residue is taken up in diethyl ether and readily soluble components are removed by filtration. Pure 3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazine-6-carboxylic acid having a melting point of 138-140°C is obtained as a crystalline product.

¹H-NMR ((CD₃)₂SO): 12.98 ppm (broad signal, OH); 11.55 ppm (s, NH); 7.66 ppm (d, 1H); 7.41 ppm (d, 1H); 4.72 ppm (s, 2H).

Example P11: 3-(2-Methyl-3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-3-oxo-propionic acid ethyl ester

1.3 g (7.3 mmol) of the potassium salt of malonic acid monomethyl ester and 0.88 g (9.2 mmol) of magnesium chloride are introduced into 20 ml of acetonitrile at 10°C, 1.5 ml (1.1 mmol) of triethylamine are added and stirring is carried out at 20°C for 1 hour. There is

then added 0.96 g (3.7 mmol) of crude 2-methyl-3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazine-6-carboxylic acid chloride ($^1\text{H-NMR}$ (CDCl_3): 8.38 ppm (broad signal, NH); 7.88 ppm (d, 1H); 7.38 ppm (d, 1H); 4.36 ppm (q, 1H); 1.63 ppm (d, 3H)), prepared from 0.82 g (4 mmol) of 2-methyl-3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazine-6-carboxylic acid (Example II.026) by heating with 0.45 ml (5 mmol) of oxalyl chloride in 15 ml of hexane and a catalytic amount of dimethylformamide, and stirring is carried out for a further 3 hours. The reaction mixture is then poured into ice-water and adjusted to pH 3 using 32 % hydrochloric acid. Extraction with ethyl acetate is carried out; washing once with 5 % sodium hydrogen carbonate solution and once with saturated sodium chloride solution and concentration by evaporation are carried out. The tautomeric forms of the desired title compound 3-hydroxy-3-(2-methyl-3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-acrylic acid ethyl ester are thereby obtained in the form of an oil. $^1\text{H-NMR}$ (CDCl_3): 8.02 ppm (broad signal, OH); 7.78 ppm (d, 1H); 7.32 ppm (d, 1H); 7.70 ppm (q, 1H); 4.18 ppm (q, 2H); 4.04 ppm (s, 1H); 1.62 ppm (d, 3H); 1.24 ppm (t, 3H).

Example P12: 6-(5-Hydroxy-1-methyl-1H-pyrazol-3-yl)-2-methyl-4H-pyrido[3,2-b][1,4]oxazin-3-one

0.82 g (2.9 mmol) of the product prepared in Example P11 is dissolved in 5 ml of acetic acid, and 0.19 ml (3.5 mmol) of methylhydrazine is added. Heating at 80°C is carried out for 4 hours and the mixture is then concentrated by evaporation. The desired 6-(5-hydroxy-1-methyl-1H-pyrazol-3-yl)-2-methyl-4H-pyrido[3,2-b][1,4]oxazin-3-one is obtained in the form of crystals by means of column chromatography (mobile phase: ethyl acetate/hexane 1/1). $^1\text{H-NMR}$ ($(\text{CD}_3)_2\text{SO}$): 11.35 ppm (s, NH); 7.58 ppm (d, 1H); 7.49 ppm (d, 1H); 5.98 ppm (s, 1H); 4.92 ppm (q, 1H); 3.71 ppm (s, 3H); 1.61 ppm (d, 3H).

Example P13: 6-(5-Difluoromethoxy-1-methyl-1H-pyrazol-3-yl)-2-methyl-4H-pyrido[3,2-b][1,4]oxazin-3-one

0.36 g (1.4 mmol) of the product prepared in Example P12 is stirred in the presence of 0.55 g (13.8 mmol) of sodium hydroxide in a mixture of 8 ml of dioxane and 8 ml of water at 70°C for 1 hour while continuously passing gaseous Freon (bromo-difluoromethane) into the mixture. The temperature is maintained at 80°C for a further 30 minutes and the mixture is then adjusted to pH 4 using hydrochloric acid and extracted with ethyl acetate. The desired 6-(5-difluoromethoxy-1-methyl-1H-pyrazol-3-yl)-2-methyl-4H-pyrido[3,2-b][1,4]oxazin-3-one is thereby obtained.

$^1\text{H-NMR}$ ($(\text{CD}_3)_2\text{SO}$): 11.60 ppm (s, NH); 7.38 ppm (d, 1H); 7.32 ppm (d, 1H); 7.26 ppm (t, 1H); 5.78 ppm (s, 1H); 4.68 ppm (q, 1H); 3.65 ppm (s, 3H); 1.34 ppm (d, 3H).

Example P14: 6-(4-Chloro-5-difluoromethoxy-1-methyl-1H-pyrazol-3-yl)-2-methyl-4H-pyrido[3,2-b][1,4]oxazin-3-one

In the presence of 0.09 g (0.11 mmol) of sodium acetate in 4 ml of acetic acid, 0.07 g (0.22 mmol) of the product prepared in Example P13 is treated, dropwise, at 60°C, with a solution of 0.015 g (0.22 mmol) of chlorine gas in acetic acid. After the reaction has terminated, the mixture is concentrated by evaporation and purified by chromatography on silica gel. The desired 6-(4-chloro-5-difluoromethoxy-1-methyl-1H-pyrazol-3-yl)-2-methyl-4H-pyrido[3,2-b][1,4]oxazin-3-one is thereby obtained.

¹H-NMR (CDCl₃): 8.45 ppm (s, NH); 7.68 ppm (d, 1H); 7.52 ppm (d, 1H); 6.68 ppm (t, 1H); 4.74 ppm (q, 1H); 3.85 ppm (s, 3H); 1.64 ppm (d, 3H).

Example P15: 2-(3-Oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-4,5,6,7-tetrahydro-isoindole-1,3-dione

1.65 g (10 mmol) of 6-amino-4H-pyrido[3,2-b][1,4]oxazin-3-one (Example P2) and 1.67 g (10 mmol) of tetrahydrophthalic acid anhydride are heated at boiling point in 10 ml of acetic acid for 7 hours. The mixture is then concentrated by evaporation and stirred in hot ethyl acetate. Pure 2-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-4,5,6,7-tetrahydro-isoindole-1,3-dione is obtained as an insoluble residue having a melting point of 220°C. ¹H-NMR (CDCl₃): 8.72 ppm (broad signal, NH); 7.38 ppm (d, 1H); 6.94 ppm (d, 1H); 4.68 ppm (s, 2H); 2.42 ppm (m, 2H); 1.80 ppm (m, 2H).

Example P16: 6-Amino-4-prop-2-ynyl-4H-pyrido[3,2-b][1,4]oxazin-3-one

4.95 g (30 mmol) of 6-amino-4H-pyrido[3,2-b][1,4]oxazin-3-one (Example P2) and 3.75 g (31 mmol) of propargyl bromide are heated at boiling point in 30 ml of acetonitrile in the presence of 4.15 g (30 mmol) of potassium carbonate and a catalytic amount of 18-crown-6 for 5 hours. The product is then extracted with ethyl acetate from an aqueous solution at pH 8 and the residue, after concentration by evaporation, is purified by chromatography. Pure 6-amino-4-prop-2-ynyl-4H-pyrido[3,2-b][1,4]oxazin-3-one having a melting point of 125.5-126°C is obtained.

Example P17: 6-Isocyanato-4-prop-2-ynyl-4H-pyrido[3,2-b][1,4]oxazin-3-one

3.5 g (17.2 mmol) of the above product from Example P16 are dissolved in 40 ml of ethyl acetate and treated with 1.87 g (9.5 mmol) of diphosgene. After the slightly exothermic reaction has subsided, the mixture is heated at 60°C for 2 hours, a clear solution being obtained. The reaction mixture is concentrated by evaporation and the crude 6-isocyanato-

4-prop-2-ynyl-4H-pyrido[3,2-b][1,4]oxazin-3-one in the form of amorphous crystals is used directly for subsequent reactions (e.g. in Example P18). For the purpose of identification, a sample of the reaction mixture is stirred in methanol in the presence of a small amount of triethylamine. According to a thin-layer chromatogram, the precipitated product is (3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-carbamic acid methyl ester.

Example P18: 7-<R,S>-Hydroxy-2-(3-oxo-4-prop-2-ynyl-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-tetrahydro-imidazo[1,5-a]pyridine-1,3-dione

0.46 g (2.3 mmol) of 4-hydroxy-piperidine-2-carboxylic acid methyl ester • hydrochloride is introduced into 15 ml of dichloromethane at 20°C. 0.50 g (5 mmol) of triethylamine is added and stirring is then carried out for 5 minutes. A dichloromethane solution of 0.54 g (2.3 mmol) of the 6-isocyanato-4-prop-2-ynyl-4H-pyrido[3,2-b][1,4]oxazin-3-one prepared above in Example P17 is then introduced dropwise and stirring is carried out at about 35°C for a further 3 hours. The reaction mixture is then concentrated by evaporation and, in order to remove insoluble components, it is filtered directly with ethyl acetate over a silica gel column. Pure 7-<R,S>-hydroxy-2-(3-oxo-4-prop-2-ynyl-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-tetrahydro-imidazo[1,5-a]pyridine-1,3-dione is obtained as an isomeric mixture having a melting point of 205.5-206°C.

Example P19: 7-<R> and 7-<S>-Fluoro-2-(3-oxo-4-prop-2-ynyl-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-tetrahydro-imidazo[1,5-a]pyridine-1,3-dione

0.16 g (0.45 mmol) of racemic 7-hydroxy-2-(3-oxo-4-prop-2-ynyl-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-tetrahydro-imidazo[1,5-a]pyridine-1,3-dione (Example P18) is treated in 5 ml of pyridine at -10°C with a solution of 0.11 g (0.68 mmol) of diethylaminosulfur trifluoride (DAST) in 1 ml of dichloromethane. The mixture is left to warm up to 20°C slowly and is stirred overnight. The mixture is then concentrated by evaporation and the aqueous solution at pH 6 is extracted with ethyl acetate, dried and concentrated by evaporation again. The first isomer, 7-<R> or 7-<S>-fluoro-2-(3-oxo-4-prop-2-ynyl-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-tetrahydro-imidazo[1,5-a]pyridine-1,3-dione, is obtained by column chromatography (mobile phase: ethyl acetate/hexane 1/1). ¹H-NMR (CDCl₃): 7.38 ppm (d, 1H); 7.04 ppm (d, 1H); 5.90 ppm (m, 1H); 4.86 ppm (m, 2H); 4.72 ppm (s, 2H). Further elution then yields the second isomer, 7-<R> or 7-<S>-fluoro-2-(3-oxo-4-prop-2-ynyl-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-tetrahydro-imidazo[1,5-a]pyridine-1,3-dione. ¹H-NMR (CDCl₃): 7.36 ppm (d, 1H); 7.01 ppm (d, 1H); 5.20 ppm (m, 1H); 4.86 ppm (m, 2H); 4.73 ppm (s, 2H).

Example P20: 1-Amino-3-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione

3.28 g (10 mmol) of 3-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione (Example P4) are stirred with 2.59 g (13 mmol) of N-2,4-dinitrophenyl-hydroxylamine in the presence of 1.22 g (14.5 mmol) of sodium hydrogen carbonate in 50 ml of dimethylformamide at 20°C for 35 hours. Water is added and extraction with ethyl acetate is carried out; the organic phase is washed twice with small amounts of water, dried over magnesium sulfate and concentrated, in part, by evaporation. The desired title compound, 1-amino-3-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione having a melting point of >220°C precipitates in the form of crystals from the ethyl acetate phase. ¹H-NMR ((CD₃)₂SO): 11.32 ppm (s, NH); 7.46 ppm (d, 1H); 6.95 ppm (d, 1H); 6.29 ppm (s, 1H); 5.48 ppm (s, NH₂); 4.68 ppm (s, 2H).

Example P21: 6-Isothiocyanato-4H-pyrido[3,2-b][1,4]oxazin-3-one

16.5 g (0.1 mol) of 6-amino-4H-pyrido[3,2-b][1,4]oxazin-3-one (Example P2) are introduced into 200 ml of ethyl methyl ketone and, over a period of 20 minutes, 13.8 g (0.12 mol) of thiophosgene are added. Stirring is then carried out at 22-28°C for 90 minutes and then 10 g (0.12 mol) of solid sodium hydrogen carbonate are first added to the mixture and then 100 ml of water are added dropwise. After the evolution of gas has ceased, stirring is continued for a further 90 minutes and extraction with 1000 ml of ethyl acetate is carried out. The aqueous phase, which contains solid components, is extracted a further three times, using 200 ml of ethyl acetate each time. The combined organic extracts are dried, filtered over Hyflo™ and concentrated until crystallisation occurs. The title compound is obtained in pure form as an ochre-coloured powder having a melting point of 178-179°C. ¹H-NMR ((CD₃)₂SO): 11.42 ppm (s, NH); 7.34 ppm (d, 1H); 6.88 ppm (d, 1H); 4.62 ppm (s, 2H).

Example P22: 6-(6-Oxo-2-thioxo-4-trifluoromethyl-3,6-dihydro-2H-pyrimidin-1-yl)-4H-pyrido[3,2-b][1,4]oxazin-3-one

3.3 g (18 mmol) of 3-amino-4,4,4-trifluoro-but-2-enoic acid ethyl ester are added dropwise at 0°C to 1.6 g (37 mmol) of sodium hydride in 15 ml of N-methylpyrrolidone as a 55 % dispersion in oil. After stirring for 15 minutes and after the evolution of hydrogen has ceased, 3.1 g (15 mmol) of 6-isothiocyanato-4H-pyrido[3,2-b][1,4]oxazin-3-one (Example P21) are added to the mixture, which is heated gradually to 90°C. After a further hour, the

mixture is cooled, water is added, the pH is adjusted to 9 and the mixture is washed twice with ethyl acetate. The aqueous phase is then acidified to pH 2 using concentrated hydrochloric acid, whereupon the product precipitates out in the form of crystals, which are filtered off and yield pure 6-(6-oxo-2-thioxo-4-trifluoromethyl-3,6-dihydro-2H-pyrimidin-1-yl)-4H-pyrido[3,2-b][1,4]oxazin-3-one having a melting point of $>220^{\circ}\text{C}$. $^1\text{H-NMR}$ ($(\text{CD}_3)_2\text{SO}$): 11.39 ppm (s, NH); 7.49 ppm (d, 1H); 7.01 ppm (d, 1H); 6.68 ppm (s, 1H); 4.72 ppm (s, 2H).

Example P23: Tetrahydro-pyridazine-1-carbothionic acid (3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-amide

9.15 g (55 mmol) of tetrahydropyridazine dihydrochloride are introduced into 150 ml of ethanol. There are then added, in succession, 11.6 g (115 mmol) of triethylamine and then, in portions, 10.4 g (50 ml) of the compound prepared in Example P21, 6-isothiocyanato-4H-pyrido[3,2-b][1,4]oxazin-3-one, the temperature being maintained between 23° and 28°C . After stirring for one hour, the precipitated product is filtered off, washed thoroughly with water and ethanol/water 1/1 and then dried *in vacuo* at 70°C . Pure tetrahydro-pyridazine-1-carbothionic acid (3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-amide having a melting point of $212\text{-}212.5^{\circ}\text{C}$ is obtained.

Example P24: 6-[3-Oxo-tetrahydro-[1,3,4]thiadiazolo[3,4-a]pyridazin-<1E>- and -<1Z>-ylideneamino]-4H-pyrido[3,2-b][1,4]oxazin-3-one and 6-(1-oxo-3-thioxo-tetrahydro-[1,2,4]triazolo[1,2-a]pyridazin-2-yl)-4H-pyrido[3,2-b][1,4]oxazin-3-one

1.47 g (5 mmol) of tetrahydro-pyridazine-1-carbothionic acid (3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-amide (Example P23) and 1.83 g (18 mmol) of triethylamine are introduced into 80 ml of tetrahydrofuran, whereupon a clear solution is obtained. At $5\text{-}10^{\circ}\text{C}$, 3.1 ml of a 20 % solution of 0.58 g (5.9 mmol) of phosgene in toluene are added slowly thereto and stirring is carried out overnight at 20°C . The solvents are distilled off under reduced pressure and the dry residue is triturated in 100 ml of water. The crystals that precipitate out are filtered off, taken up while hot in 80 ml of fresh tetrahydrofuran and poorly soluble components are removed by filtering again. Pure 6-[3-oxo-tetrahydro-[1,3,4]thiadiazolo[3,4-a]pyridazin-<1E>- or -<1Z>-ylideneamino]-4H-pyrido[3,2-b][1,4]oxazin-3-one (= product A, Example 12.001) having a melting point of $>225^{\circ}\text{C}$ is thereby obtained. $^1\text{H-NMR}$ ($(\text{CD}_3)_2\text{SO}$): 11.40 ppm (s, NH); 7.51 ppm (d, 1H); 6.81 ppm (d, 1H); 4.78 ppm (s, 2H); 3.97 ppm (m, 2H); 3.75 ppm (m, 2H); 1.90 ppm (m, 4H).

The mother liquor is concentrated by evaporation and yields, after filtration over silica gel (mobile phase hexane/tetrahydrofuran 3/2), approx. 80 % 6-(1-oxo-3-thioxo-tetrahydro-[1,2,4]triazolo[1,2-a]pyridazin-2-yl)-4H-pyrido[3,2-b][1,4]oxazin-3-one having a melting point

of >225°C (= product B), which is contaminated with approx. 20 % product A. ¹H-NMR ((CD₃)₂SO): 11.50 ppm (s, NH); 7.68 ppm (d, 1H); 7.21 ppm (d, 1H); 4.91 ppm (s, 2H); 4.56 ppm (m, 2H); 3.68 ppm (m, 2H); 2.02 ppm (m, 4H).

Example P25: 6-[3-Oxo-tetrahydro-[1,3,4]thiadiazolo[3,4-a]pyridazin-<1E>- and/or -<1Z>-ylideneamino]-4-prop-2-ynyl-4H-pyrido[3,2-b][1,4]oxazin-3-one and 6-(1-oxo-3-thioxo-tetrahydro-[1,2,4]triazolo[1,2-a]pyridazin-2-yl)-4-prop-2-ynyl-4H-pyrido[3,2-b][1,4]oxazin-3-one
0.35 g (1.1 mmol) of the 4/1 mixture of product B isolated in Example P24 is heated at boiling point in the presence of 0.15 g (1.3 mmol) of propargyl bromide, 0.18 g (1.3 mmol) of potassium carbonate and a catalytic amount of 18-crown-6 in 10 ml of acetonitrile and 3 ml of N-methylpyrrolidone for 2.5 hours. The mixture is then concentrated by evaporation and the residue is chromatographed on silica gel (mobile phase ethyl acetate/hexane 1/1); pure 6-[3-oxo-tetrahydro-[1,3,4]thiadiazolo[3,4-a]pyridazin-<1E>- and/or -<1Z>-ylideneamino]-4-prop-2-ynyl-4H-pyrido[3,2-b][1,4]oxazin-3-one is first isolated as product A having a melting point of >225°C. ¹H-NMR ((CD₃)₂SO): 7.28 ppm (d, 1H); 6.78 ppm (d, 1H); 4.92 ppm (d, 2H); 4.68 ppm (s, 2H); 3.90 ppm (m, 2H); 3.74 ppm (m, 2H); 2.20 ppm (t, 2H); 1.90 ppm (m, 4H). Pure 6-(1-oxo-3-thioxo-tetrahydro-[1,2,4]triazolo[1,2-a]pyridazin-2-yl)-4-prop-2-ynyl-4H-pyrido[3,2-b][1,4]oxazin-3-one having a melting point of >225°C is isolated thereafter as main product B. ¹H-NMR ((CD₃)₂SO): 7.41 ppm (d, 1H); 7.13 ppm (d, 1H); 4.88 ppm (d, 2H); 4.77 ppm (s, 2H); 4.04 ppm (m, 2H); 3.74 ppm (m, 2H); 2.17 ppm (t, 2H); 1.98 ppm (m, 4H).

Example P26: (3-Oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-thiocarbamic acid O-ethyl ester

15.5 g (75 mmol) of 6-isothiocyanato-4H-pyrido[3,2-b][1,4]oxazin-3-one (Example P21) are heated in 300 ml of absolute ethanol at boiling point for 1 hour. From the reaction mixture, which has been cooled to 10°C, there can be obtained pure (3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-thiocarbamic acid O-ethyl ester having a melting point of 218.5-219°C.

Example P27: 6-(4,5-Dihydro-1H-imidazol-2-ylamino)-4H-pyrido[3,2-b][1,4]oxazin-3-one

5.7 g (20 mmol) of (3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-thiocarbamic acid O-ethyl ester (Example P26) are heated in 20 ml of ethylenediamine at 80°C for 90 minutes. The solid product that precipitates out is pure 6-(4,5-dihydro-1H-imidazol-2-ylamino)-4H-pyrido[3,2-b][1,4]oxazin-3-one having a melting point of >225°C.

Example P28: 6-(7-Oxo-5-trifluoromethyl-2,3-dihydro-7H-imidazo[1,2-a]pyrimidin-8-yl)-4H-pyrido[3,2-b][1,4]oxazin-3-one

3.3 g (14.1 mmol) of 6-(4,5-dihydro-1H-imidazol-2-ylamino)-4H-pyrido[3,2-b][1,4]oxazin-3-one (Example P27) and 3.2 g (16.3 mmol) of 3-amino-4,4,4-trifluoro-but-2-enoic acid ethyl ester are heated in 12 ml of N-methylpyrrolidone at 135°C for 8 hours. Water is added thereto and extraction is carried out several times with warm ethyl acetate. From the combined organic phases there crystallises, on concentration by evaporation, pure 6-(7-oxo-5-trifluoromethyl-2,3-dihydro-7H-imidazo[1,2-a]pyrimidin-8-yl)-4H-pyrido[3,2-b][1,4]oxazin-3-one having a melting point of >225°C. ¹H-NMR ((CD₃)₂SO): 11.46 ppm (s, NH); 7.56 ppm (d, 1H); 7.06 ppm (d, 1H); 6.02 ppm (s, 1H), 4.69 ppm (s, 2H), 4.22 ppm (t, 2H); 3.80 ppm (t, 3H).

Example P29: 6-(2-Methyl-7-oxo-5-trifluoromethyl-2,3-dihydro-7H-imidazo[1,2-a]pyrimidin-8-yl)-4-(1-methyl-prop-2-ynyl)-4H-pyrido[3,2-b][1,4]oxazin-3-one

0.31 g (0.85 mmol) of 6-(2-methyl-7-oxo-5-trifluoromethyl-2,3-dihydro-7H-imidazo[1,2-a]pyrimidin-8-yl)-4H-pyrido[3,2-b][1,4]oxazin-3-one (Example 11.002) and 0.28 g (0.19 mmol) of 3-mesyloxy-but-1-yne are heated in the presence of approx. 0.23 g (1.9 mmol) of potassium carbonate and a catalytic amount of 18-crown-6 in 10 ml of tetrahydrofuran and 5 ml of N-methylpyrrolidone in a small pressure reactor at an internal temperature of 110°C for 4 hours. The reaction mixture is then extracted from an aqueous phase by shaking with ethyl acetate and is separated by chromatography over silica gel using ethyl acetate/methanol 9/1 as mobile phase into the two racemic <S,S> or <R,R> and <S,R> or <R,S> isomers of 6-(2-methyl-7-oxo-5-trifluoromethyl-2,3-dihydro-7H-imidazo[1,2-a]pyrimidin-8-yl)-4-(1-methyl-prop-2-ynyl)-4H-pyrido[3,2-b][1,4]oxazin-3-one. Isomer I: ¹H-NMR (CDCl₃): 7.32 ppm (d, 1H); 7.02 ppm (d, 1H); 6.04 ppm (qxd, 1H); 5.84 ppm (s, 1H); 5.88 ppm (s, 1H); 4.68 ppm (s, 2H), 4.2 ppm (m, 2H); 3.58 ppm (m, 1H); 2.52 ppm (m, 1H); 1.61 ppm (d, 3H); 1.30 ppm (m, 3H). Isomer II: ¹H-NMR (CDCl₃): 7.40 ppm (d, 1H); 6.98 ppm (d, 1H); 5.94 ppm (qxd, 1H); 5.88 ppm (s, 1H); 4.69 ppm (s, 2H), 4.2 ppm (m, 2H); 3.65 ppm (m, 1H); 2.30 ppm (m, 1H); 1.72 ppm (dxd, 3H); 1.30 ppm (m, 3H).

Example P30: 3-(4-n-Propyl-3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-5-chloro-1-methyl-6-trifluoromethyl-1H-pyrimidine-2,4-dione

0.17 g (0.44 mmol) of 3-(4-n-propyl-3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-1-methyl-6-trifluoromethyl-1H-pyrimidine-2,4-dione (Example 1.060) is treated, in the presence of 0.15 g (1.7 mmol) of sodium acetate in 5 ml of acetic acid at 40°C, with chlorine gas until all the starting material has completely reacted. Extraction with ethyl acetate is

then carried out; washing once with sodium acetate solution, drying and recrystallisation are carried out. Pure 3-(4-n-propyl-3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-5-chloro-1-methyl-6-trifluoromethyl-1H-pyrimidine-2,4-dione having a melting point of 176-178°C is thereby obtained. ¹H-NMR (CDCl₃): 7.38 ppm (d, 1H); 6.87 ppm (d, 1H); 4.72 ppm (s, 2H), 4.01 ppm (m, 2H); 3.62 ppm (s, 3H); 1.67 ppm (m, 2H); 0.90 ppm (t, 3H).

Example P31: 6-(2-Fluoromethoxy-6-oxo-4-trifluoromethyl-6H-pyrimidin-1-yl)-4-prop-2-ynyl-4H-pyrido[3,2-b][1,4]oxazin-3-one and 1-fluoromethyl-3-(3-oxo-4-prop-2-ynyl-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione

0.19 g (0.52 mmol) of 3-(3-oxo-4-prop-2-ynyl-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione (Example 1.006) is introduced into 5 ml of dimethylformamide in the presence of 0.09 g (0.67 mmol) of potassium carbonate and, at 0°C, is treated with 0.25 ml of bromofluoromethane. The mixture is left to warm up to 20°C overnight, with vigorous stirring; the reaction mixture is then taken up in diethyl ether and the diethyl ether phase is washed once with dilute hydrochloric acid and once with sodium chloride solution. The residue is concentrated by evaporation and then separated by HPLC (mobile phase gradient from 30 to 40 % ethyl acetate in hexane) into two products, there being obtained, as less polar component, 6-(2-fluoromethoxy-6-oxo-4-trifluoromethyl-6H-pyrimidin-1-yl)-4-prop-2-ynyl-4H-pyrido[3,2-b][1,4]oxazin-3-one having ¹H-NMR (CDCl₃): 7.46 ppm (d, 1H); 6.98 ppm (d, 1H); 6.72 ppm (s, 1H); 5.95 ppm (d, J=50Hz, 1H); 4.82 ppm (4H); 2.12 ppm (t, 1H), and, as more polar component, 1-fluoromethyl-3-(3-oxo-4-prop-2-ynyl-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione having a melting point of 192-193°C and ¹H-NMR (CDCl₃): 7.41 ppm (d, 1H); 6.95 ppm (d, 1H); 6.45 ppm (s, 1H); 6.01 ppm (d, J=50Hz, 1H); 4.82 ppm (d, 2H); 4.78 ppm (s, 2H); 2.14 ppm (t, 1H).

Example P32: 1-Amino-3-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione

1.77 g (4.9 mmol) of 1-methylthio-3-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione (compound no. 2.002) is dissolved in 15 ml chloroform and treated with 2.44 g (9.8 mmol) m-chloroperbenzoic acid stirring and maintaining the temperature at below 30 °C. After 3 hours, according to thin layer chromatography the 1-methylsulfonyl-3-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione (compound no. 2.008) can be detected only, the reaction mixture is added under stirring to an ice-cold solution of 25% ammoniumhydroxide. After 5 minutes the crystals formed are filtered, washed with water and dried yielding

technical grade 1-amino-3-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione with a melting point of $>250^{\circ}\text{C}$. $^1\text{H-NMR}$ ($(\text{CD}_3)_2\text{SO}$): 10.65 ppm (broad signal, NH); 7.38 ppm (d, 1H); 7.3 ppm (broad signal, NH_2); 6.92 ppm (d, 1H); 6.02 ppm (s, 1H); 4.62 ppm (s, 2H).

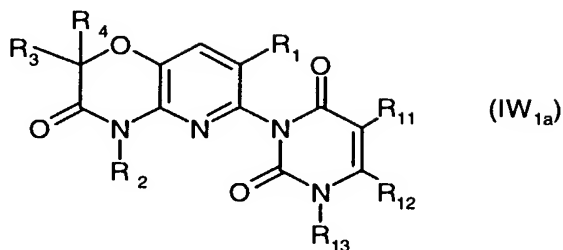
Example P33: 6-(7-Oxo-5-trifluoromethyl-7H-imidazo[1,2-a]pyrimidin-8-yl)-4H-pyrido[3,2-b][1,4]oxazin-3-one

1.15 g (3.5 mmol) 1-amino-3-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-trifluoromethyl-1H-pyrimidine-2,4-dione (Example P32) is added to a well-stirred mixture of 1 ml 32% hydrochloric acid and 5 ml acetic acid containing 1.12 g (7.0 mmol) bromoacetaldehyde and heated afterwards for 17 hours to refluxing temperature. The cold solution is acidified to pH 3 and extracted with ethylacetate. The organic phase is washed once with sodiumbicarbonate solution and evaporated. By HPLC the pure 6-(7-oxo-5-trifluoromethyl-7H-imidazo[1,2-a]pyrimidin-8-yl)-4H-pyrido[3,2-b][1,4]oxazin-3-one is obtained. $^1\text{H-NMR}$ ($(\text{CD}_3)_2\text{SO}$): 11.23 ppm (s, NH); 7.35 ppm (d, 1H); 7.32 ppm (b, 1H); 6.91 ppm (d, 1H); 6.88 ppm (b, 1H); 6.78 ppm (s, 1H); 4.53 ppm (s, 2H).

Example P34: 1,5-Dimethyl-3-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-thioxo-[1,3,5]triazinane-2,4-dione

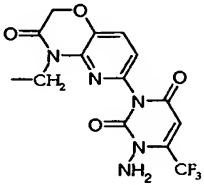
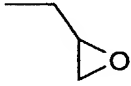

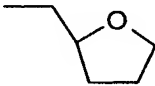
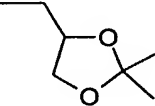
0.57 g (2 mmol) (3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-carbamic acid phenyl ester (compound no. II.029) is added to a solution of 0.22 g (2 mmol) N,N'-dimethylthiourea in 10 ml NMP containing a catalytic amount of triethylamine. After 5 minutes 0.65 g (4 mmol) carbonyldiimidazole is added and the mixture heated for 6 hours to 80°C . Then once again 0.65 g (4 mmol) carbonyldiimidazole is added and the mixture stirred further overnight at 95°C . The reaction mixture is poured into icewater and the crystals of almost pure 1,5-dimethyl-3-(3-oxo-3,4-dihydro-2H-pyrido[3,2-b][1,4]oxazin-6-yl)-6-thioxo-[1,3,5]triazinane-2,4-dione are filtered off and dried. $^1\text{H-NMR}$ ($(\text{CD}_3)_2\text{SO}$): 11.58 ppm (s, NH); 7.68 ppm (d, 1H); 7.22 ppm (d, 1H); 4.88 ppm (s, 2H); 3.72 ppm (s, 6H).

The preferred compounds listed in the following Tables 1, 2, 4, 5, 7, 11, 12 and 100 can also be obtained in analogous manner or using methods described in the Reaction Schemes and in the mentioned references.

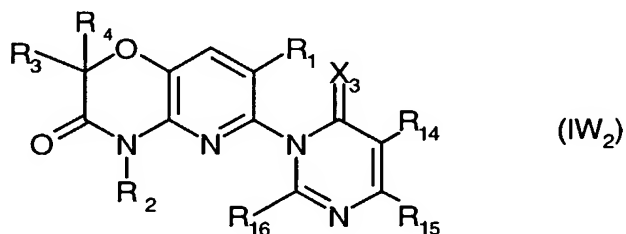
Table 1: Compounds of formula IW_{1a}

comp. no. (Example)	R ₁	R ₂	R ₃	R ₄	R ₁₁	R ₁₂	R ₁₃	physical data
1.001 (P4)	H	H	H	H	H	CF ₃	H	>220°C
1.002 (P6)	H	H	H	H	H	CF ₃	CH ₃	>220°C
1.003 (P5)	H	CH ₃	H	H	H	CF ₃	CH ₃	211-212°C
1.004 (P8)	H	isopropyl	H	H	H	CF ₃	CH ₃	solid
1.005 (P7)	H	CH ₂ C≡CH	H	H	H	CF ₃	CH ₃	161-162°C
1.006	H	CH ₂ C≡CH	H	H	H	CF ₃	H	183-184°C
1.007	H	CH ₂ C≡CH	H	H	H	CF ₃	CH ₂ C≡CH	amorphous crystals
1.008	H	CH ₂ CH ₃	H	H	H	CF ₃	H	205-206°C
1.009	H	H	H	H	H	CF ₃	CH ₂ CH ₃	220°C
1.010	H	CH ₂ CH ₃	H	H	H	CF ₃	CH ₂ CH ₃	resin
1.011	H	CH ₂ C≡CH	H	H	H	CF ₃	CH ₂ CH ₃	169-170°C
1.012	H	CH ₂ CH ₃	H	H	H	CF ₃	CH ₃	191-192°C
1.013	H	CH ₂ CH=CH ₂	H	H	H	CF ₃	CH ₃	133-135°C
1.014	H	isobutyl	H	H	H	CF ₃	CH ₃	resin
1.015	H	sec-butyl	H	H	H	CF ₃	CH ₃	amorphous crystals
1.016	H	CH(CH ₃)C≡CH	H	H	H	CF ₃	CH ₃	amorphous crystals
1.017	H	CH ₂ C≡N	H	H	H	CF ₃	CH ₃	208-209°C
1.018	H	CH ₂ CH ₂ OCH ₃	H	H	H	CF ₃	CH ₃	154-155°C
1.019	H	CH ₂ CCl=CH ₂	H	H	H	CF ₃	CH ₃	amorphous crystals
1.020	H	CH(CH ₃)CH=CH ₂	H	H	H	CF ₃	CH ₃	amorphous crystals
1.021	H	CH ₂ SCH ₃	H	H	H	CF ₃	CH ₃	resin
1.022	H		H	H	H	CF ₃	CH ₃	resin
1.023	H	CH ₂ CH=CHCH ₃	H	H	H	CF ₃	CH ₃	amorphous crystals
1.024	H		H	H	H	CF ₃	CH ₃	109-110°C, 166-167°C (dual melting point)
1.025	H	CH ₂ CH ₂ CH(OCH ₃) ₂	H	H	H	CF ₃	CH ₃	resin
1.026	H	3-MeO-benzyl	H	H	H	CF ₃	CH ₃	resin
1.027	H	CH ₂ C(CH ₃)=CH ₂	H	H	H	CF ₃	CH ₃	144-145°C
1.028	H	CH ₂ C(O)OCH ₂ CH ₂ OCH ₃	H	H	H	CF ₃	CH ₃	resin
1.029	H	4-Cl-benzyl	H	H	H	CF ₃	CH ₃	amorphous crystals
1.030	H	4-benzyloxy-benzyl	H	H	H	CF ₃	CH ₃	resin
1.031	H	3-phenoxy-benzyl	H	H	H	CF ₃	CH ₃	resin
1.032	H	CH ₂ CH=C(CH ₃)Cl	H	H	H	CF ₃	CH ₃	resin
1.033	H	CH ₂ CH ₂ CH ₂ Cl	H	H	H	CF ₃	CH ₃	resin

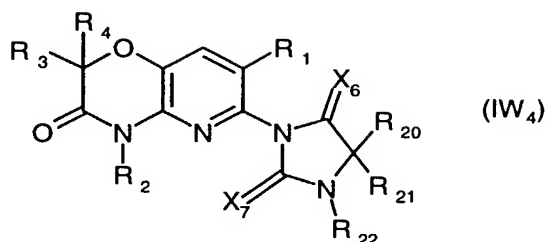
1.034	H	CH ₂ CH ₂ CH ₂ CH ₂ Cl	H	H	H	CF ₃	CH ₃	resin
1.035	H	CH ₂ CH(CH ₃)CH ₂ Cl	H	H	H	CF ₃	CH ₃	resin
1.036	H	CH ₂ C(O)OC(CH ₃) ₃	H	H	H	CF ₃	CH ₃	resin
1.037	H	4-MeO-benzyl	H	H	H	CF ₃	CH ₃	amorphous crystals
1.038	H	CH ₂ C(O)C(CH ₃) ₃	H	H	H	CF ₃	CH ₃	resin
1.039	H	2-Cl-benzyl	H	H	H	CF ₃	CH ₃	resin
1.040	H	CH ₂ CH ₂ CF=CF ₂	H	H	H	CF ₃	CH ₃	amorphous crystals
1.041	H	CH ₂ CH ₂ CH ₂ F	H	H	H	CF ₃	CH ₃	resin
1.042	H	CH ₂ CH=CHC≡CC(CH ₃) ₃	H	H	H	CF ₃	CH ₃	resin
1.043	H	CH ₂ CH ₂ -phenyl	H	H	H	CF ₃	CH ₃	amorphous crystals
1.044	H	H	n-butyl	H	H	CF ₃	H	>225°C
1.045	H	H	CH ₂ CH ₃	H	H	CF ₃	H	>225°C
1.046	H	H	CH ₃	H	H	CF ₃	H	>225°C
1.047	H	H	CH ₃	H	H	CF ₃	CH ₃	>230°C
1.048	H	H	CH ₂ CH ₃	H	H	CF ₃	CH ₃	>230°C
1.049	H	H	n-butyl	H	H	CF ₃	CH ₃	208-209°C
1.049	H	CH ₂ CH ₃	n-butyl	H	H	CF ₃	CH ₃	resin
1.050	H	CH ₂ C≡CH	n-butyl	H	H	CF ₃	CH ₃	122-123°C
1.051	H	CH ₂ CH=CH ₂	n-butyl	H	H	CF ₃	CH ₃	102-103°C
1.052	H	CH ₂ CH=CH ₂	CH ₂ CH ₃	H	H	CF ₃	CH ₃	75-76°C
1.053	H	CH ₂ C≡CH	CH ₂ CH ₃	H	H	CF ₃	CH ₃	109-110°C
1.054	H	CH ₂ C≡CH	CH ₃	H	H	CF ₃	CH ₃	79-80°C
1.055	H	CH ₂ CH=CH ₂	CH ₃	H	H	CF ₃	CH ₃	115-116°C
1.056	H	CH ₂ CH ₃	CH ₃	H	H	CF ₃	CH ₃	135-136°C
1.057	H	CH(CH ₃) ₂	CH ₃	H	H	CF ₃	CH ₃	104-105°C
1.058	H	CH ₂ CH ₂ CH ₃	CH ₃	H	H	CF ₃	CH ₃	110-111°C
1.059	H	CH ₂ CF ₃	CH ₃	H	H	CF ₃	CH ₃	180-181°C
1.060	H	CH ₂ CH ₂ CH ₃	H	H	H	CF ₃	CH ₃	146-147°C
1.061	H	CH ₂ CH ₂ CH ₂ =CH ₂	H	H	H	CF ₃	CH ₃	143-144°C
1.062 (P20)	H	H	H	H	H	CF ₃	NH ₂	>220°C
1.063	H	CH ₂ C≡CH	H	H	H	CF ₃	NH ₂	114-115°C
1.064	H	CH ₂ CH=CH ₂	H	H	H	CF ₃	NH ₂	94°C
1.065	H	CH ₂ CF ₃	H	H	H	CF ₃	CH ₃	resin
1.066	H	CH ₂ CH ₃	H	H	H	CF ₃	NH ₂	165-167°C
1.067	H	CH ₃	H	H	H	CF ₃	NH ₂	> 220°C
1.068	H	CH(CH ₃)C≡CH	H	H	H	CF ₃	NH ₂	89°C (decomposition)
1.069	H	CH ₂ CH ₂ CH ₃	H	H	H	CF ₃	NH ₂	amorphous crystals
1.070	H	CH ₂ C(O)CH ₂ CH ₃	H	H	H	CF ₃	NH ₂	163-164°C
1.071	H	CH ₂ C(O)CH ₂ CH ₃	H	H	H	CF ₃	CH ₃	203-204°C
1.072	H	CH ₂ C(O)-cyclopropyl	H	H	H	CF ₃	CH ₃	202-203°C
1.073	H	CH ₂ CH(OCH ₃) ₂	H	H	H	CF ₃	CH ₃	177-178°C
1.074	H	CH ₂ CH ₂ Cl	H	H	H	CF ₃	CH ₃	154-155°C
1.075	H	CH ₂ C(O)C(CH ₃) ₃	H	H	H	CF ₃	NH ₂	resin
1.076	H	CH ₂ C(O)OC(CH ₃) ₃	H	H	H	CF ₃	NH ₂	resin
1.077	H	CH ₂ CH=CH(Cl)CH ₃	H	H	H	CF ₃	NH ₂	resin
1.078	H	CH ₂ CH ₂ CH ₂ Cl	H	H	H	CF ₃	NH ₂	resin
1.079	H	CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ Cl	H	H	H	CF ₃	NH ₂	resin

1.080	H		H	H	H	CF ₃	NH ₂	amorphous crystals
1.081	H	CH ₂ Si(CH ₃) ₂ CH ₂ CH ₃	H	H	H	CF ₃	NH ₂	resin
1.082	H	CH ₂ CH ₂ CH ₂ CH ₂ Cl	H	H	H	CF ₃	NH ₂	resin
1.083	H	CH ₂ CH(CH ₃)CH ₂ Cl	H	H	H	CF ₃	NH ₂	resin
1.084	H	CH ₂ CH ₂ CH ₂ CH=CH ₂	H	H	H	CF ₃	NH ₂	resin
1.085	H	CH ₂ CH ₂ CH ₂ F	H	H	H	CF ₃	NH ₂	147.5-148°C
1.086	H	CH ₂ C(CH ₂ Si(CH ₃) ₃)=CH ₂	H	H	H	CF ₃	NH ₂	resin
1.087	H	CH ₂ CH=CHC≡CC(CH ₃) ₃	H	H	H	CF ₃	NH ₂	resin
1.088	H	CH ₂ C(Br)=CH ₂	H	H	H	CF ₃	NH ₂	resin
1.089	H	CH(CH ₂ CH ₃)C(O)OCH ₃	H	H	H	CF ₃	NH ₂	resin
1.090	H		H	H	H	CF ₃	NH ₂	resin
1.091	H	CH ₂ CH ₂ CH(CH ₃) ₂	H	H	H	CF ₃	NH ₂	resin
1.092	H		H	H	H	CF ₃	NH ₂	resin
1.093	H	CH ₂ CH ₂ CH ₂ C≡N	H	H	H	CF ₃	NH ₂	resin
1.094	H	CH ₂ CH ₂ OCH ₂ CH ₂ OCH ₃	H	H	H	CF ₃	NH ₂	amorphous crystals
1.095	H	CH ₂ CH=CHCH ₃	H	H	H	CF ₃	NH ₂	amorphous crystals
1.096	H	CH ₂ CH=CHC(O)OCH ₃	H	H	H	CF ₃	NH ₂	resin
1.097	H	CH ₂ C(CH ₃)=CH ₂	H	H	H	CF ₃	NH ₂	resin
1.098	H	CH ₂ CH ₂ CH=C(CH ₃) ₂	H	H	H	CF ₃	NH ₂	amorphous crystals
1.099	H	CH ₂ CH ₂ CH ₂ C≡CH	H	H	H	CF ₃	NH ₂	resin
1.100	H	n-nonyl	H	H	H	CF ₃	NH ₂	resin
1.101	H	CH ₂ CH ₂ CH(Cl)CH ₃	H	H	H	CF ₃	NH ₂	resin
1.102	H		H	H	H	CF ₃	NH ₂	resin
1.103	H	CH ₂ CH(CH ₂ CH ₃) ₂	H	H	H	CF ₃	NH ₂	resin
1.104	H	CH ₂ CHF ₂	H	H	H	CF ₃	NH ₂	resin
1.105	H		H	H	H	CF ₃	NH ₂	resin
1.106	H	cyclohexyl	H	H	H	CF ₃	NH ₂	resin
1.107 (P30)	H	CH ₂ CH ₂ CH ₃	H	H	Cl	CF ₃	CH ₃	110-111°C

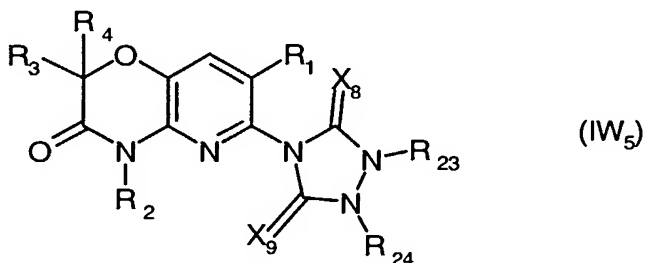
1.108	H	CH(CH ₃) ₂	H	H	H	CF ₃	NH ₂	¹ H-NMR (CDCl ₃): 7.37 ppm (d, 1H); 6.88 ppm (d, 1H); 6.28 ppm (s, 1H); 5.18 ppm (q, 1H); 4.62 ppm (s, 2H); 4.58 ppm (s, NH ₂); 1.51 ppm (d, 6H).
1.109 (P31)	H	CH ₂ C≡CH	H	H	H	CF ₃	CH ₂ F	191-193°C
1.110	H	CH ₂ CH ₂ CH ₂ CH ₃	H	H	H	CF ₃	CH ₃	147-148°C
1.111	H	CH ₂ CH=C(CH ₃) ₂	H	H	H	CF ₃	CH ₃	141-142°C
1.112	H	CH ₂ CH=CHCH ₂ CH ₃	H	H	H	CF ₃	CH ₃	141-142°C, <Z>-isomer
1.113	H	CH ₂ CH=CHCH ₂ CH ₃	H	H	H	CF ₃	CH ₃	141-142°C, <E>-isomer
1.114	H	CH ₂ CH ₂ CH ₂ CH=CH ₂	H	H	H	CF ₃	CH ₃	154°C

Table 2: Compounds of formula IW₂

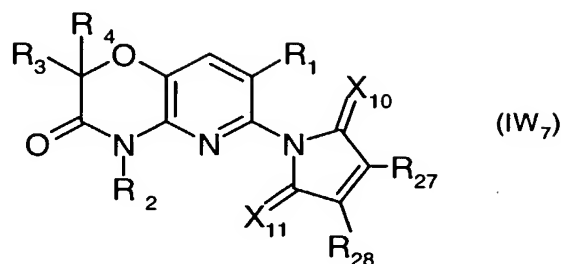
comp. no. (Example)	R ₁	R ₂	R ₃	R ₄	X ₃	R ₁₄	R ₁₅	R ₁₆	physical data, remarks
2.001 (P22)	H	H	H	H	O	H	CF ₃	SH	>220°C, tautomeric form IW ₁₉
2.002	H	H	H	H	O	H	CF ₃	SCH ₃	>206°C
2.003	H	CH ₃	H	H	O	H	CF ₃	SCH ₃	>220°C
2.004	H	CH ₂ CH=CH ₂	H	H	O	H	CF ₃	SCH ₃	143-144°C
2.005	H	CH ₂ C≡CH	H	H	O	H	CF ₃	SCH ₃	183-184°C
2.006	H	CH ₂ CH ₂ CH ₃	H	H	O	H	CF ₃	SCH ₃	128-129°C
2.007 (P31)	H	CH ₂ C≡CH	H	H	O	H	CF ₃	OCH ₂ F	resin
2.008	H	H	H	H	O	H	CF ₃	SO ₂ CH ₃	¹ H-NMR (DMSO-D ₆): 11.41 ppm (s, 1H); 7.45 ppm (d, 1H); 7.37 ppm (s, 1H); 7.07 ppm (d, 1H); 4.67 ppm (s, 2H); 3.32 ppm (s, 3H).
2.009 (P32)	H	H	H	H	O	H	CF ₃	NH ₂	>250°C

Table 4: Compounds of formula IW₄

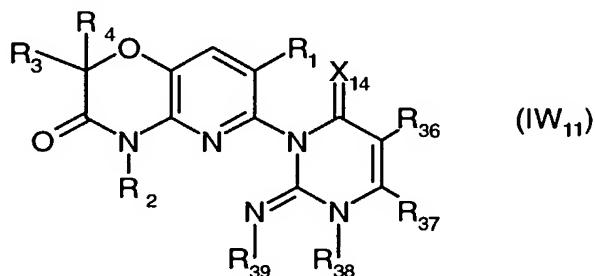
comp. no. (Example)	R ₁	R ₂	R ₃	R ₄	X ₆	X ₇	R ₂₀	R ₂₁	R ₂₂	physical data
4.001	H	H	H	H	O	O	H	-CH ₂ CH(OH)CH ₂ CH ₂ -		225°C (isomer I)
4.002	H	H	H	H	O	O	H	-CH ₂ CH(OH)CH ₂ CH ₂ -		225°C (isomer II)
4.003 (P18)	H	CH ₂ C≡CH	H	H	O	O	H	-CH ₂ CH(OH)CH ₂ CH ₂ -		205.5-206°C
4.004 (P19)	H	CH ₂ C≡CH	H	H	O	O	H	-CH ₂ CH(F)CH ₂ CH ₂ -		205°C (isomer I)
4.005 (P19)	H	CH ₂ C≡CH	H	H	O	O	H	-CH ₂ CH(F)CH ₂ CH ₂ -		205°C (isomer II)

Table 5: Compounds of formula IW₅

comp. no. (Example)	R ₁	R ₂	R ₃	R ₄	X ₈	X ₉	R ₂₃	R ₂₄	physical data
5.001 (P24)	H	H	H	H	S	O	-CH ₂ CH ₂ CH ₂ CH ₂ -		>225°C
5.002 (P25)	H	CH ₂ C≡CH	H	H	S	O	-CH ₂ CH ₂ CH ₂ CH ₂ -		>225°C
5.003	H	CH ₂ CH=CH ₂	H	H	S	O	-CH ₂ CH ₂ CH ₂ CH ₂ -		186-187°C
5.004	H	CH ₂ CH ₂ CH ₃	H	H	S	O	-CH ₂ CH ₂ CH ₂ CH ₂ -		210-210.5°C
5.005	H	CH ₂ CH ₃	H	H	S	O	-CH ₂ CH ₂ CH ₂ CH ₂ -		197-197.5°C
5.006	H	H	H	H	S	O	-CH ₂ CH ₂ OCH ₂ CH ₂ -		>225°C
5.007	H	CH ₂ CH=CH ₂	H	H	S	O	-CH ₂ CH ₂ OCH ₂ CH ₂ -		192-193°C
5.008	H	CH ₂ C≡CH	H	H	S	O	-CH ₂ CH ₂ OCH ₂ CH ₂ -		>225°C
5.009	H	CH ₂ CH ₂ CH ₃	H	H	S	O	-CH ₂ CH ₂ OCH ₂ CH ₂ -		172-173°C
5.010	H	CH ₂ CH ₃	H	H	S	O	-CH ₂ CH ₂ OCH ₂ CH ₂ -		223-224°C
5.011	H	CH ₂ CH ₂ CH ₂ CH ₃	H	H	S	O	-CH ₂ CH ₂ CH ₂ CH ₂ -		153-154°C
5.012	H	CH ₂ CH ₂ CH=CH ₂	H	H	S	O	-CH ₂ CH ₂ CH ₂ CH ₂ -		153-154°C
5.013	H	CH ₂ CH ₂ CH ₂ CH=CH ₂	H	H	S	O	-CH ₂ CH ₂ CH ₂ CH ₂ -		177-178°C

Table 7: Compounds of formula IW₇

comp. no. (Example)	R ₁	R ₂	R ₃	R ₄	R ₂₇	R ₂₈	X ₁₀	X ₁₁	physical data
7.001	H	CH ₂ C≡CH	H	H	-CH ₂ CH ₂ CH ₂ CH ₂ -	O	O	O	181-182°C
7.002	H	CH(CH ₃)C≡CH	H	H	-CH ₂ CH ₂ CH ₂ CH ₂ -	O	O	O	69-70°C
7.003	H	isopropyl	H	H	-CH ₂ CH ₂ CH ₂ CH ₂ -	O	O	O	137-138°C
7.004	H	CH ₂ CH=CHCl (cis)	H	H	-CH ₂ CH ₂ CH ₂ CH ₂ -	O	O	O	resin
7.005	H	CH ₂ CH=CHCl (trans)	H	H	-CH ₂ CH ₂ CH ₂ CH ₂ -	O	O	O	141-142°C
7.006	H	benzyl	H	H	-CH ₂ CH ₂ CH ₂ CH ₂ -	O	O	O	178-179°C
7.007 (P15)	H	H	H	H	-CH ₂ CH ₂ CH ₂ CH ₂ -	O	O	O	220°C
7.008	H	H	H	H	-CH=CH-CH=CH-	O	O	O	>220°C
7.009	H	CH ₂ C≡CH	H	H	-CH=CH-CH=CH-	O	O	O	>220°C
7.010	H	CH ₂ CH=CH ₂	H	H	-CH=CH-CH=CH-	O	O	O	183-184°C

Table 11: Compounds of formula IW₁₁

comp. no. (Example)	R ₁	R ₂	R ₃	R ₄	X ₁₄	R ₃₆	R ₃₇	R ₃₈	R ₃₉	physical data, remarks
11.001 (P28)	H	H	H	H	O	H	CF ₃	-CH ₂ CH ₂ -		>225°C
11.002	H	H	H	H	O	H	CF ₃	-CH ₂ CH(CH ₃)-		>225°C
11.003	H	CH ₂ C≡CH	H	H	O	H	CF ₃	-CH ₂ CH ₂ -		223-224°C
11.004	H	CH ₂ CH=CH ₂	H	H	O	H	CF ₃	-CH ₂ CH ₂ -		152-153°C
11.005	H	CH ₂ CH ₂ CH ₃	H	H	O	H	CF ₃	-CH ₂ CH ₂ -		137-137.5°C
11.006	H	CH ₂ CH ₃	H	H	O	H	CF ₃	-CH ₂ CH ₂ -		159.5-160°C
11.007	H	CH(CH ₃)C≡CH	H	H	O	H	CF ₃	-CH ₂ CH ₂ -		206.5-207.5°C
11.008	H	CH ₂ C≡CH	H	H	O	H	CF ₃	-CH ₂ CH(CH ₃)-		191-191.5°C
11.009	H	CH ₂ CH=CH ₂	H	H	O	H	CF ₃	-CH ₂ CH(CH ₃)-		143-143.5°C
11.010	H	CH ₂ CH ₃	H	H	O	H	CF ₃	-CH ₂ CH(CH ₃)-		115-117°C, 126-128°C (dual melting point)
11.011	H	CH ₂ CH ₂ CH ₃	H	H	O	H	CF ₃	-CH ₂ CH(CH ₃)-		122-122.5°C


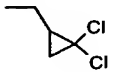
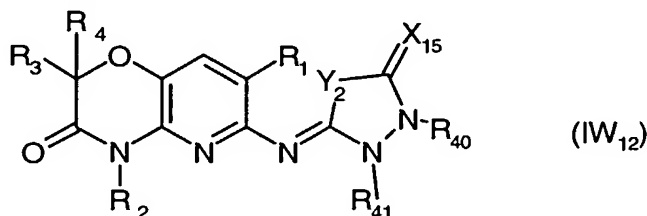
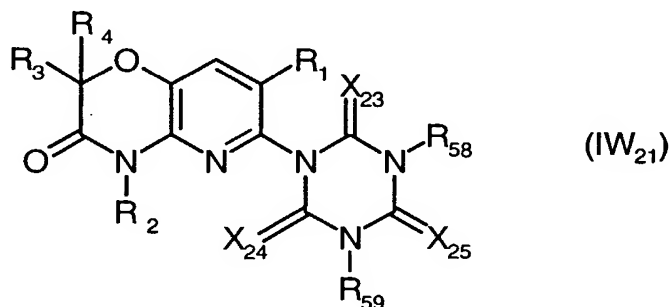
11.012 (P29)	H	CH(CH ₃)C≡CH	H	H	O	H	CF ₃	-CH ₂ CH(CH ₃).	resin, isomer I
11.013 (P29)	H	CH(CH ₃)C≡CH	H	H	O	H	CF ₃	-CH ₂ CH(CH ₃).	>200°C (decomp.), isomer II
11.014	H	CH ₂ C(O)C(CH ₃) ₃	H	H	O	H	CF ₃	-CH ₂ CH ₂ .	resin
11.015	H	CH ₂ C(O)OC(CH ₃) ₃	H	H	O	H	CF ₃	-CH ₂ CH ₂ .	resin
11.016	H	CH ₂ CH=C(Cl)CH ₃	H	H	O	H	CF ₃	-CH ₂ CH ₂ .	resin, <E>/<Z>-mixture
11.017	H	CH ₂ CH ₂ CH ₂ Cl	H	H	O	H	CF ₃	-CH ₂ CH ₂ .	resin
11.018	H	CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ Cl	H	H	O	H	CF ₃	-CH ₂ CH ₂ .	resin
11.019	H	CH ₂ Si(CH ₃) ₂ CH ₂ CH ₃	H	H	O	H	CF ₃	-CH ₂ CH ₂ .	resin
11.020	H	CH ₂ CH(CH ₃)CH ₂ Cl	H	H	O	H	CF ₃	-CH ₂ CH ₂ .	resin
11.021	H	CH ₂ CH ₂ CH ₂ CH=CH ₂	H	H	O	H	CF ₃	-CH ₂ CH ₂ .	resin
11.022	H	CH ₂ CH ₂ CH ₂ F	H	H	O	H	CF ₃	-CH ₂ CH ₂ .	resin
11.023	H	CH ₂ C(=CH ₂)CH ₂ Si(CH ₃) ₃	H	H	O	H	CF ₃	-CH ₂ CH ₂ .	resin
11.024	H	CH ₂ CH=CHC≡CC(CH ₃) ₃	H	H	O	H	CF ₃	-CH ₂ CH ₂ .	resin
11.025	H	CH ₂ C(O)CH ₂ CH ₃	H	H	O	H	CF ₃	-CH ₂ CH ₂ .	resin
11.026	H	CH ₂ C(Br)=CH ₂	H	H	O	H	CF ₃	-CH ₂ CH ₂ .	resin
11.027	H	CH ₂ CH(COOCH ₃)CH ₂ CH ₃	H	H	O	H	CF ₃	-CH ₂ CH ₂ .	resin
11.028	H		H	H	O	H	CF ₃	-CH ₂ CH ₂ .	resin
11.029	H	CH ₂ CH ₂ CH(CH ₃) ₂	H	H	O	H	CF ₃	-CH ₂ CH ₂ .	resin
11.030	H		H	H	O	H	CF ₃	-CH ₂ CH ₂ .	resin
11.031	H	CH ₂ CH ₂ CH ₂ C≡N	H	H	O	H	CF ₃	-CH ₂ CH ₂ .	resin
11.032	H	CH ₂ CH ₂ OCH ₂ CH ₂ OCH ₃	H	H	O	H	CF ₃	-CH ₂ CH ₂ .	resin
11.033	H	CH(CH ₃)CH=CH ₂	H	H	O	H	CF ₃	-CH ₂ CH ₂ .	resin
11.034	H	CH ₂ CH=CHCOOCH ₃	H	H	O	H	CF ₃	-CH ₂ CH ₂ .	resin
11.035	H	CH ₂ C(CH ₃)=CH ₂	H	H	O	H	CF ₃	-CH ₂ CH ₂ .	resin
11.036	H	CH ₂ CH ₂ CH=C(CH ₃) ₂	H	H	O	H	CF ₃	-CH ₂ CH ₂ .	resin
11.037 (P33)	H	H	H	H	O	H	CF ₃	-CH=CH-	>225°C
11.038	H	CH ₂ C≡CH	H	H	O	H	CF ₃	-CH=CH-	208-210 °C

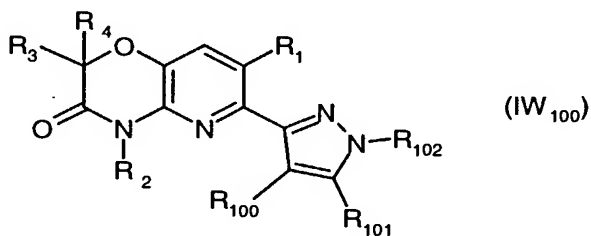
Table 12: Compounds of formula IW₁₂

comp. no. (Example)	R ₁	R ₂	R ₃	R ₄	Y ₂	X ₁₅	R ₄₀	R ₄₁	physical data
12.001 (P24)	H	H	H	H	S	O	-CH ₂ CH ₂ CH ₂ CH ₂ -		>225°C, <E> or <Z> isomer
12.002 (P25)	H	CH ₂ C≡CH	H	H	S	O	-CH ₂ CH ₂ CH ₂ CH ₂ -		>225°C, <E> or <Z> isomer
12.003	H	CH ₂ CH=CH ₂	H	H	S	O	-CH ₂ CH ₂ CH ₂ CH ₂ -		197-198°C, <E> or <Z> isomer
12.004	H	CH ₂ CH ₂ CH ₃	H	H	S	O	-CH ₂ CH ₂ CH ₂ CH ₂ -		188-189°C, <E> or <Z> isomer

12.005	H	CH ₂ CH ₃	H	H	S	O	-CH ₂ CH ₂ CH ₂ CH ₂ -	>220°C, <E> or <Z> isomer
12.006	H	H	H	H	S	O	-CH ₂ CH ₂ OCH ₂ CH ₂ -	>225°C, <E> or <Z> isomer
12.007	H	CH ₂ CH=CH ₂	H	H	S	O	-CH ₂ CH ₂ OCH ₂ CH ₂ -	221-22°C, <E> or <Z> isomer
12.008	H	CH ₂ C≡CH	H	H	S	O	-CH ₂ CH ₂ OCH ₂ CH ₂ -	>225°C, <E> or <Z> isomer
12.009	H	CH ₂ CH ₂ CH ₃	H	H	S	O	-CH ₂ CH ₂ OCH ₂ CH ₂ -	214-215°C, <E> or <Z> isomer
12.010	H	CH ₂ CH ₂ CH ₂ CH ₃	H	H	S	O	-CH ₂ CH ₂ CH ₂ CH ₂ -	129-130°C, <E> or <Z> isomer
12.011	H	CH ₂ CH ₂ CH=CH ₂	H	H	S	O	-CH ₂ CH ₂ CH ₂ CH ₂ -	154-165°C, <E> or <Z> isomer
12.012	H	CH ₂ CH ₂ CH ₂ CH=CH ₂	H	H	S	O	-CH ₂ CH ₂ CH ₂ CH ₂ -	141-142°C, <E> or <Z> isomer

Table 21: Compounds of formula IW₂₁

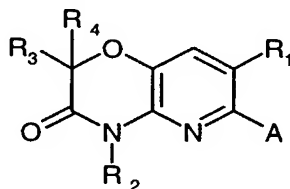
comp. no. (Example)	R ₁	R ₂	R ₃	R ₄	X ₂₃	X ₂₄	X ₂₅	R ₅₈	R ₅₉	physical data
21.001 (P34)	H	H	H	H	O	O	S	CH ₃	CH ₃	>225°C
21.002	H	CH ₂ C≡CH	H	H	O	O	S	CH ₃	CH ₃	
21.003	H	CH ₂ CH=CH ₂	H	H	O	O	S	CH ₃	CH ₃	

Table 100: Compounds of formula IW₁₀₀

comp. no. (Example)	R ₁	R ₂	R ₃	R ₄	R ₁₀₀	R ₁₀₁	R ₁₀₂	physical data
100.001	F	CH ₂ C≡CH	H	H	Cl	OCHF ₂	CH ₃	127-128°C
100.002	F	CH ₃	H	H	Cl	OCHF ₂	CH ₃	138-139°C
100.003 (P9)	F	H	H	H	Cl	OCHF ₂	CH ₃	solid
100.004	F	isopropyl	H	H	Cl	OCHF ₂	CH ₃	123-124°C
100.005	F	CH(CH ₃)COOCH ₃	H	H	Cl	OCHF ₂	CH ₃	93-95°C
100.006	F	CH ₂ CH ₂ SCH ₂ CH ₃	H	H	Cl	OCHF ₂	CH ₃	oil

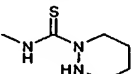
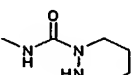
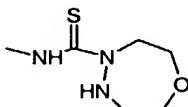
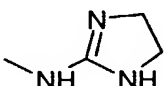
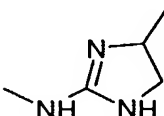
100.007 (P13)	H	H	H	CH ₃	H	OCHF ₂	CH ₃	solid
100.008 (P14)	H	H	H	CH ₃	Cl	OCHF ₂	CH ₃	solid
100.009 (P12)	H	H	H	CH ₃	H	OH	CH ₃	solid; tautomeric form IW _{100z}

Table II: Compounds of formula II:



(II)

comp. no. (Example)	R ₁	R ₂	R ₃	R ₄	A	physical data
II.001 (P1)	H	H	H	H	NO ₂	247-252°C
II.002 (P2)	H	H	H	H	NH ₂	279-281°C
II.003 (P21)	H	H	H	H	N=C=S	178-179°C
II.004	Br	H	H	H	NO ₂	solid
II.005	Cl	H	H	H	Cl	solid
II.006	Cl	H	H	H	NO ₂	206-207°C
II.007	H	H	CH ₃	H	NO ₂	186-187°C
II.008	H	H	n-butyl	H	NO ₂	solid
II.009	H	H	CH ₃	H	N=C=S	solid
II.010	H	H	n-butyl	H	NH ₂	>235°C
II.011	H	H	n-butyl	H	N=C=S	solid
II.012	H	H	n-butyl	H	NHCSNHC(CH ₃) ₃	solid
II.013	H	H	CH ₃	H	NH ₂	>230°C
II.014	H	H	H	H	NHCSNHC(CH ₃) ₃	solid
II.015	H	H	n-decyl	H	N=C=S	solid
II.016	Cl	H	n-butyl	H	NO ₂	solid
II.017	H	H	CH ₂ CH ₃	H	CH ₃	solid
II.018	H	H	CH ₃	CH ₃	CH ₃	solid
II.019	Cl	H	CH ₂ CH ₃	H	CH ₃	solid
II.020	Cl	H	CH ₃	H	CH ₃	solid
II.021	Cl	H	CH ₃	CH ₃	CH ₃	solid
II.022	Cl	H	n-butyl	H	N=C=S	solid
II.023	H	H	2,4-Cl ₂ -6-NO ₂ -phenyl	H	NO ₂	solid
II.024	H	H	H	H	Br	solid
II.025 (P10)	H	H	H	H	COOH	138-140°C
II.026	H	H	CH ₃	H	COOH	H-NMR ((CD ₃) ₂ SO): 11.80 ppm (s, NH); 7.68 ppm (d, 1H); 7.45 ppm (d, 1H); 4.88 ppm (q, 1H); 1.47 ppm (d, 3H).
II.027 (P11)	H	H	CH ₃	H	COCH ₂ COOEt	oil
II.028	Br	H	H	H	NH ₂	220°C
II.029	H	H	H	H	NHCOO-phenyl	>225°C
II.030 (P16)	H	CH ₂ C≡CH	H	H	NH ₂	125-126°C

II.031	(P17)	H	CH ₂ C≡CH	H	H	N=C=O	amorphous crystals
II.032	(P17)	H	CH ₂ C≡CH	H	H	NHCOOMe	amorphous crystals
II.033	(P3)	H	H	H	H	NHCOOEI	220°C
II.034		Cl	H	H	H	NH ₂	>230°C
II.035		H	H	H	H	Cl	180-181°C
II.036		H	CH ₂ C≡CH	H	H	NHCOOEI	154-155°C
II.037		H	H	CH ₃	H	NHCOOEI	>220°C
II.038		H	H	CH ₂ CH ₃	H	NHCOOEI	>225°C
II.039		H	H	n-butyl	H	NHCOOEI	>220°C
II.040		Cl	H	H	H	NHCOOC(CH ₃) ₃	amorphous crystals
II.041		H	CH ₂ CH ₃	H	H	NH ₂	95°C
II.042		H	CH ₂ CH=CH ₂	H	H	NH ₂	91°C
II.043		H	CH ₂ CH=CH ₂	H	H	NHCOOEI	100-101°C
II.044		H	H	H	H	NHCOOCH ₂ CH(CH ₃) ₂	232-234°C
II.045		H	CH ₂ CH=CH ₂	H	H	OH	112-113°C
II.046		H	CH ₂ CF ₃	H	H	NH ₂	resin
II.047		H	CH ₂ CF ₃	H	H	NHCOOEI	resin
II.048	(P23)	H	H	H	H		212-212.5°C
II.049		H	H	H	H		> 220°C
II.050		H	H	H	H		212.5-213°C
II.051	(P26)	H	H	H	H	NHC(S)OEI	218-219°C
II.052	(P27)	H	H	H	H		>225°C
II.053		H	H	H	H		>225°C
II.054		H	CH ₂ C≡CH	H	H	N=C=S	135-136°C
II.055		Br	H	H	H	Br	230-232°C
II.056		Br	CH ₂ CH ₃	H	H	Br	115-116°C
II.057		H	CH ₂ CH ₃	H	H	Cl	76-77°C
II.058		H	H	CH ₂ CH ₃	H	NO ₂	182-183°C
II.059		H	H	CH ₂ CH ₃	H	NH ₂	231-232°C

Biological Examples:

Example B1: Herbicidal action before emergence of the plants (pre-emergence action)

Monocotyledonous and dicotyledonous test plants are sown in standard soil in plastics pots. Immediately after sowing, the test compounds, in the form of an aqueous suspension (prepared from a 25 % wettable powder (Example F3, b) according to WO 97/34485), or in the form of an emulsion (prepared from a 25 % emulsifiable concentrate (Example F1, c) according to WO 97/34485), are applied by spraying in a concentration corresponding to 250 g of active ingredient/ha (500 litres water/ha). The test plants are then grown in a greenhouse under optimum conditions. After a test duration of 3 weeks, the test is evaluated in accordance with a scale of nine ratings (1 = total damage, 9 = no action). Ratings of from 1 to 4 (especially from 1 to 3) indicate good to very good herbicidal action.

Test plants: Setaria, Panicum, Digitaria, Sida, Ipomea, Amaranthus, Chenopodium, Stellaria, Veronica.

The compounds according to the invention exhibit good herbicidal action.

Examples of the good herbicidal action of compounds of formula I are given in Table B1.

Table B1: Pre-emergence action (at 250 g a.i./ha)

[illegible]

1.052	1	1	1	1	3	1	4	5	1
1.053	1	1	1	1	1	1	1	4	1
1.054	1	1	1	1	1	1	1	1	1
1.055	1	1	1	1	1	1	1	5	1
1.056	1	1	1	1	1	1	1	1	1
1.057	1	1	1	1	1	1	1	1	1
1.058	1	1	1	1	2	1	1	1	1
1.059	1	1	1	1	1	1	1	5	1
1.060	1	1	1	1	1	1	1	1	1
1.061	2	2	1	1	2	1	3	3	1
1.063	1	1	1	1	1	1	1	1	1
1.064	1	1	1	1	1	1	1	1	1
1.065	1	1	1	1	1	1	1	4	1
1.066	1	1	1	1	1	1	1	1	1
1.067	1	1	1	1	1	1	1	1	1
1.068	1	1	1	1	1	1	1	1	1
1.069	1	1	1	1	1	1	1	1	1
1.070	1	1	1	1	1	1	1	1	1
1.071	1	1	1	1	1	1	1	1	1

The same results are obtained when the compounds of formula I are formulated in accordance with Examples F2 and F4 to F8 according to WO 97/34485.

Example B2: Post-emergence herbicidal action

In a greenhouse, monocotyledonous and dicotyledonous test plants are grown in standard soil in plastics pots and at the 4- to 6-leaf stage are sprayed with an aqueous suspension of the test compounds of formula I, prepared from a 25 % wettable powder (Example F3, b) according to WO 97/34485), or with an emulsion of the test compounds of formula I, prepared from a 25 % emulsifiable concentrate (Example F1, c) according to WO 97/34485), in a concentration corresponding to 250 g of active ingredient/ha (500 litres water/ha). The test plants are then grown on in a greenhouse under optimum conditions. After a test duration of about 18 days, the test is evaluated in accordance with a scale of nine ratings (1 = total damage, 9 = no action). Ratings of from 1 to 4 (especially from 1 to 3) indicate good to very good herbicidal action.

Test plants: Setaria, Panicum, Digitaria, Euphorbia, Ipomea, Amaranthus, Chenopodium, Polygonum, Veronica.

In this test too, the compounds of formula I exhibit strong herbicidal action.

Examples of the good herbicidal action of compounds of formula I are given in Table B2.

Table B2: Post-emergence action (at 250 g of a.i./ha)

comp. no.	Setaria	Panicum	Digitaria	Euphorbia	Ipomea	Amaranthu s	Chenopodium	Polygonum	Veronica
100.001	2	1	4	1	1	1	1	1	1
100.002	2	2	4	2	1	1	2	1	1
100.003	2	1	2	1	1	1	1	1	1
100.004	4	5	6	1	1	3	2	1	1
100.005	4	1	3	1	1	2	1	1	1
100.006	3	2	4	1	1	1	2	1	1
1.003	2	1	2	2	1	1	1	2	1
1.004	1	1	1	1	1	1	1	1	1
1.005	1	1	1	1	1	1	1	1	1
7.001	2	1	2	1	1	1	1	1	1
7.002	1	1	1	1	1	1	1	2	1
7.003	5	1	7	1	1	1	1	1	1
7.004	7	2	8	2	1	1	1	1	1
4.004	9	4	8	2	1	1	1	1	1
1.012	1	1	1	2	1	1	1	1	1
1.013	1	1	1	2	1	1	1	1	1
1.014	2	1	1	2	1	1	1	1	1
1.015	1	1	1	2	1	1	1	1	1
1.016	2	1	2	2	1	1	1	1	1
1.017	6	1	3	2	1	1	1	1	1
1.018	2	1	2	2	1	1	1	1	1
1.019	3	1	2	3	1	1	1	-	1
1.020	2	1	1	1	1	1	1	-	1
1.022	1	1	1	1	1	1	1	-	1
1.023	1	1	1	2	1	1	1	-	1
1.024	1	1	1	1	1	1	1	-	1
1.025	7	2	7	3	1	3	1	-	1
1.026	7	1	4	3	1	1	2	-	1
1.027	3	1	2	1	1	1	1	-	1
1.032	4	1	7	1	2	1	3	-	1
1.033	2	1	1	1	1	1	1	-	1
1.034	1	1	2	2	1	2	1	-	1
1.035	5	1	4	1	1	1	1	-	1
1.041	2	1	1	1	1	1	1	-	1
1.042	1	2	5	3	1	1	2	-	1
1.048	7	3	7	3	2	2	2	-	3
1.052	2	1	3	2	2	2	3	-	1
1.053	2	1	3	1	1	1	1	-	1
1.054	2	1	1	1	1	1	1	-	1
1.055	2	1	1	2	1	1	1	-	1
1.056	2	1	2	2	1	1	1	-	1
1.057	2	1	1	1	1	1	1	-	1
1.058	2	1	2	1	1	1	1	-	1
1.059	2	2	2	2	1	2	1	-	1
1.060	1	1	1	2	1	1	1	1	1
1.061	2	1	2	2	1	1	1	1	1
1.062	4	1	1	3	1	1	1	1	1
1.063	1	1	1	1	1	1	1	1	1
1.064	1	1	1	1	1	1	1	1	1
1.065	1	1	1	2	1	1	1	1	1

1.066	1	1	1	1	1	1	1	1	1
1.067	1	1	1	2	1	1	1	1	1
1.068	1	1	1	1	1	1	1	1	1
1.069	1	1	1	1	1	1	1	1	1
1.070	2	1	2	2	1	1	1	1	1
1.071	2	1	1	2	1	1	1	1	1
1.072	1	1	1	3	1	1	1	1	1
1.073	3	1	1	2	1	1	1	1	1
1.074	1	1	1	2	1	1	1	1	1
12.002	3	4	6	2	1	1	3	1	1
5.002	4	2	6	1	1	1	1	1	1
11.003	2	1	1	2	1	1	1	1	1
11.004	4	1	1	2	1	2	1	1	1
11.005	1	1	1	2	1	1	1	1	1
11.006	3	2	3	2	1	2	1	1	1
5.003	4	4	4	1	1	1	1	1	1
1.107	1	1	1	1	1	2	1	1	1
5.004	3	2	2	1	1	1	1	1	1
5.005	2	2	4	2	1	1	1	1	1
1.075	3	1	3	2	1	3	2	1	1
1.077	1	1	1	1	1	1	1	1	1
1.078	1	1	1	1	1	1	1	1	1
1.079	1	1	1	2	1	1	1	1	1
1.081	5	3	6	3	3	1	1	1	2
1.082	1	1	1	2	1	1	1	1	1
1.083	1	1	1	1	1	1	1	1	1
1.084	1	1	1	2	1	1	1	1	1
1.085	1	1	1	1	1	1	1	1	1
1.086	2	1	1	1	1	1	1	1	1
1.087	3	1	2	2	1	4	1	1	1
1.088	1	1	1	2	1	1	1	1	1
1.089	1	1	1	2	1	1	1	1	1
1.090	5	1	3	2	1	1	1	1	1
1.091	1	1	1	2	1	1	1	1	1
1.092	1	1	1	2	2	1	1	1	1

The same results are obtained when the compounds of formula I are formulated in accordance with Examples F2 and F4 to F8 according to WO 97/34485.

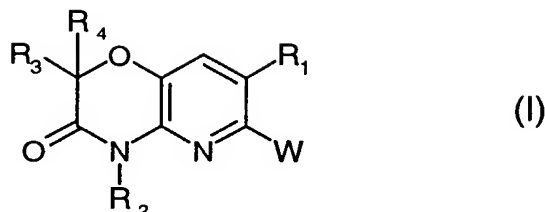
The compounds of formula I according to the invention can also be used for weed control in admixture with known herbicides as co-herbicides, for example in the form of ready-prepared formulations or in the form of a 'tank-mix'. Suitable mixing partners for the compounds of formula I include, for example, the following co-herbicides: compound of formula I + acetochlor; compound of formula I + acifluorfen; compound of formula I + aclonifen; compound of formula I + alachlor; compound of formula I + ametryn; compound of formula I + aminotriazole; compound of formula I + amidosulfuron; compound of formula I + asulam; compound of formula I + atrazine; compound of formula I + BAY FOE 5043; compound of formula I + benazolin; compound of formula I + bensulfuron; compound of

formula I + bentazone; compound of formula I + bifenox; compound of formula I + bispyribac-sodium; compound of formula I + bialaphos; compound of formula I + bromacil; compound of formula I + bromoxynil; compound of formula I + bromophenoxim; compound of formula I + butachlor; compound of formula I + butylate; compound of formula I + cafenstrole; compound of formula I + carbetamide; compound of formula I + chloridazone; compound of formula I + chlorimuron-ethyl; compound of formula I + chlorbromuron; compound of formula I + chlorsulfuron; compound of formula I + chlortoluron; compound of formula I + cinosulfuron; compound of formula I + clethodim; compound of formula I + clodinafop; compound of formula I + clomazone; compound of formula I + clopyralid; compound of formula I + cloransulam; compound of formula I + cyanazine; compound of formula I + cyhalofop; compound of formula I + dalapon; compound of formula I + 2,4-D; compound of formula I + 2,4-DB; compound of formula I + desmetryn; compound of formula I + desmedipham; compound of formula I + dicamba; compound of formula I + diclofop; compound of formula I + difenzoquat metilsulfate; compound of formula I + diflufenican; compound of formula I + dimefuron; compound of formula I + dimepiperate; compound of formula I + dimethachlor; compound of formula I + dimethametryn; compound of formula I + dimethenamid; compound of formula I + S-dimethenamid; compound of formula I + dinitramine; compound of formula I + dinoterb; compound of formula I + dipropetryn; compound of formula I + diuron; compound of formula I + diquat; compound of formula I + DSMA; compound of formula I + EPTC; compound of formula I + esprocarb; compound of formula I + ethalfluralin; compound of formula I + ethametsulfuron; compound of formula I + ethephon; compound of formula I + ethofumesate; compound of formula I + ethoxysulfuron; compound of formula I + fenclorim; compound of formula I + flamprop; compound of formula I + fluazasulfuron; compound of formula I + fluazifop; compound of formula I + flumetralin; compound of formula I + flumetsulam; compound of formula I + fluometuron; compound of formula I + flurochloridone; compound of formula I + fluoxaprop; compound of formula I + fluroxypyr; compound of formula I + fluthiacet-methyl; compound of formula I + fluxofenim; compound of formula I + fomesafen; compound of formula I + glufosinate; compound of formula I + glyphosate; compound of formula I + halosulfuron; compound of formula I + haloxyfop; compound of formula I + hexazinone; compound of formula I + imazamethabenz; compound of formula I + imazapyr; compound of formula I + imazaquin; compound of formula I + imazethapyr; compound of formula I + imazosulfuron; compound of formula I + ioxynil; compound of formula I + isoproturon; compound of formula I + isoxaben; compound of formula I + isoxaflutole; compound of formula I + karbutylate; compound of formula I + lactofen; compound of formula I + lenacil; compound of formula I + linuron; compound of formula I + MCPP; compound of formula I + metamitron;

compound of formula I + metazachlor; compound of formula I + methabenzthiazuron; compound of formula I + methazole; compound of formula I + metobromuron; compound of formula I + metolachlor; compound of formula I + S-metolachlor; compound of formula I + metosulam; compound of formula I + metribuzin; compound of formula I + metsulfuron-methyl; compound of formula I + molinate; compound of formula I + MCPA; compound of formula I + MSMA; compound of formula I + napropamide; compound of formula I + NDA-402989; compound of formula I + nefenacet; compound of formula I + nicosulfuron; compound of formula I + norflurazon; compound of formula I + oryzalin; compound of formula I + oxadiazon; compound of formula I + oxasulfuron; compound of formula I + oxyfluorfen; compound of formula I + paraquat; compound of formula I + pendimethalin; compound of formula I + phenmedipham; compound of formula I + phenoxaprop-P-ethyl (R); compound of formula I + picloram; compound of formula I + pretilachlor; compound of formula I + primisulfuron; compound of formula I + prometon; compound of formula I + prometryn; compound of formula I + propachlor; compound of formula I + propanil; compound of formula I + propazine; compound of formula I + propaquizafop; compound of formula I + propyzamide; compound of formula I + prosulfuron; compound of formula I + pyrazolynate; compound of formula I + pyrazosulfuron-ethyl; compound of formula I + pyrazoxyphen; compound of formula I + pyridate; compound of formula I + pyriminobac-methyl; compound of formula I + pyrithiobac-sodium; compound of formula I + quinclorac; compound of formula I + quizalofop; compound of formula I + rimsulfuron; compound of formula I + sequestrene; compound of formula I + sethoxydim; compound of formula I + simetryn; compound of formula I + simazine; compound of formula I + sulcotrione; compound of formula I + sulfosate; compound of formula I + sulfosulfuron-methyl; compound of formula I + tebutam; compound of formula I + tebuthiuron; compound of formula I + terbacil; compound of formula I + terbumeton; compound of formula I + terbuthylazine; compound of formula I + terbutryn; compound of formula I + thiazafluron; compound of formula I + thiazopyr; compound of formula I + thifensulfuron-methyl; compound of formula I + thiobencarb; compound of formula I + tralkoxydim; compound of formula I + triallate; compound of formula I + triasulfuron; compound of formula I + trifluralin; compound of formula I + tribenuron-methyl; compound of formula I + triclopyr; compound of formula I + triflusulfuron; and compound of formula I + trinexapac-ethyl, and esters and salts of those mixing partners for the compound of formula I that are mentioned e.g. in The Pesticide Manual, Eleventh Edition, 1997, BCPC.

What is claimed is:

1. A compound of formula I



wherein

R_1 is hydrogen, methyl or halogen;

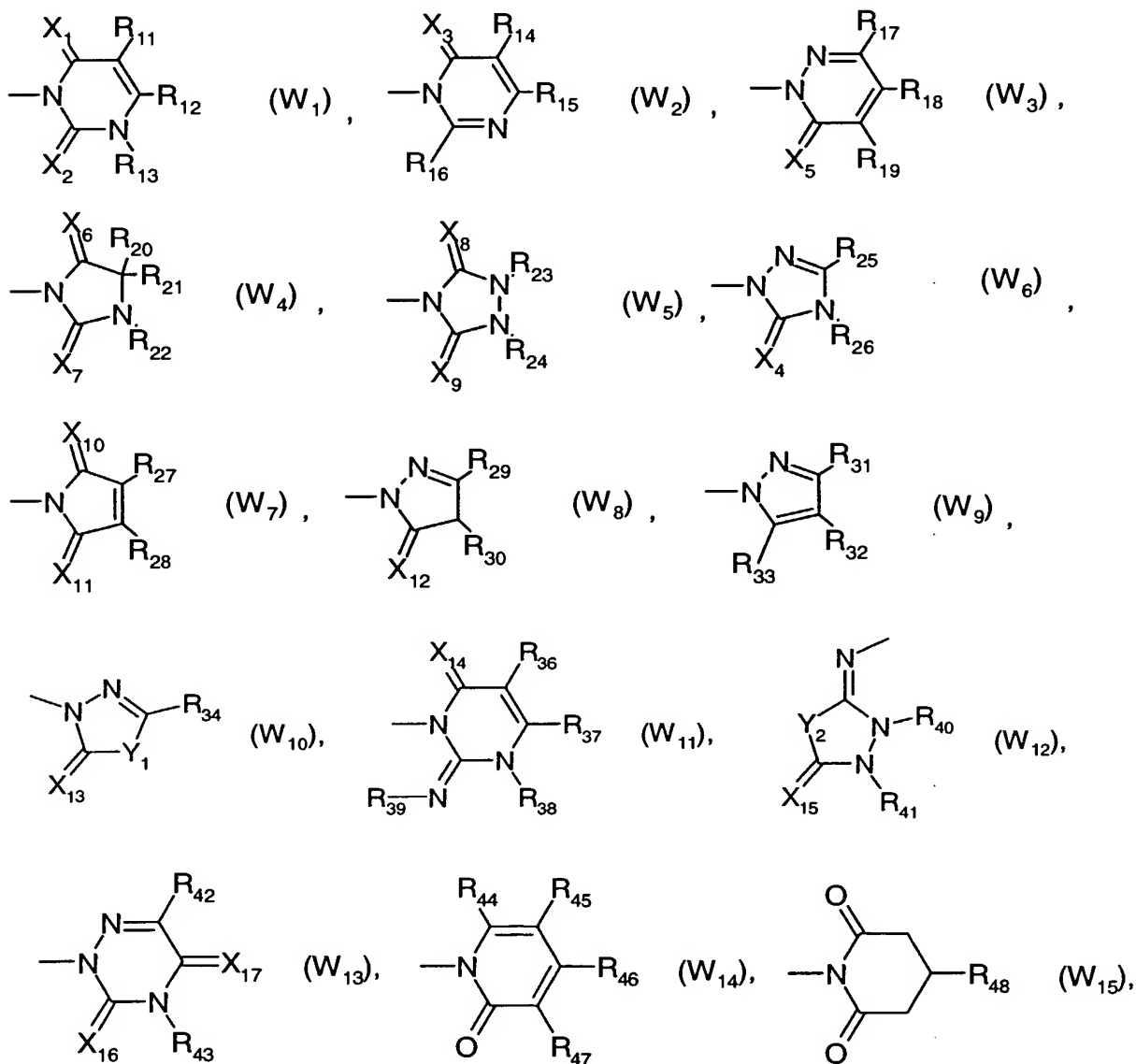
R_2 is hydrogen, C_1 - C_{12} alkyl, C_1 - C_{12} haloalkyl, C_2 - C_{12} alkenyl, C_2 - C_{12} alkynyl, C_2 - C_8 alkynyl- C_2 - C_4 alkenyl, C_3 - C_{12} allenyl, C_2 - C_{12} haloalkenyl, C_2 - C_{12} haloalkynyl, C_3 - C_6 cycloalkyl, C_3 - C_6 cycloalkyl- C_1 - C_4 alkyl, C_3 - C_6 halocycloalkyl- C_1 - C_4 alkyl, tri(C_1 - C_4 alkyl)silyl- C_1 - C_4 alkyl, tri(C_1 - C_4 alkyl)silyl- C_2 - C_4 alkenyl, cyano- C_1 - C_{12} alkyl, C_1 - C_6 alkoxy- C_1 - C_4 alkyl, C_1 - C_4 alkoxy- C_1 - or - C_2 -alkoxy- C_1 - or - C_2 -alkyl, di(C_1 - C_4 alkoxy)- C_1 - or - C_2 -alkyl, ethylenedioxy- C_1 - or - C_2 -alkyl, C_2 - C_6 alkenyloxy- C_1 - C_4 alkyl, C_2 - C_6 haloalkenyloxy- C_1 - C_4 alkyl, C_2 - C_6 alkynyloxy- C_1 - C_4 alkyl, C_3 - C_6 haloalkynyloxy- C_1 - C_4 alkyl, C_1 - C_6 alkylthio- C_1 - C_4 alkyl, C_1 - C_6 alkylsulfinyl- C_1 - C_4 alkyl, C_1 - C_6 alkylsulfonyl- C_1 - C_4 alkyl, hydroxy- C_1 - C_{12} alkyl, C_1 - C_6 alkylcarbonyl- C_1 - C_4 alkyl, C_1 - C_6 haloalkylcarbonyl- C_1 - C_4 alkyl, C_1 - C_6 alkoxycarbonyl- C_1 - C_4 alkyl, C_1 - C_6 alkoxy- C_1 - or - C_2 -alkoxycarbonyl- C_1 - C_4 alkyl, C_1 - C_6 alkoxycarbonyl- C_1 - C_4 haloalkyl, C_3 - C_6 cycloalkylcarbonyl- C_1 - C_4 alkyl or benzoyl- C_1 - C_4 alkyl wherein the benzoyl group may be substituted by halogen, C_1 - C_3 alkyl, C_1 - C_3 haloalkyl, C_1 - C_3 alkoxy or by C_1 - C_3 haloalkoxy, or is C_3 - C_6 alkenyloxycarbonyl- C_1 - C_4 alkyl, C_3 - C_6 alkynyloxycarbonyl- C_1 - C_4 alkyl, C_1 - C_6 alkylcarbonyloxy- C_1 - C_4 alkyl, C_2 - C_6 alkenylcarbonyloxy- C_1 - C_4 alkyl, C_3 - C_6 cycloalkylcarbonyloxy- C_1 - C_4 alkyl, benzoyloxy- C_1 - C_4 alkyl, C_1 - C_6 alkoxycarbonyloxy- C_1 - C_4 alkyl, carbamoyl- C_1 - C_4 alkyl, C_1 - C_6 alkylaminocarbonyl- C_1 - C_4 alkyl, or phenyl- or heterocyclyl-substituted C_1 - C_4 alkyl, wherein the phenyl and heterocyclyl groups may be substituted by halogen, C_1 - C_6 alkyl, C_1 - C_6 alkoxy, C_1 - C_6 haloalkyl, C_1 - C_6 haloalkoxy, C_2 - C_6 alkenyl, C_2 - C_6 alkynyl, C_2 - C_6 haloalkenyl, C_2 - C_6 haloalkynyl, C_3 - C_6 cycloalkyl- C_1 - C_4 alkyl, C_3 - C_6 halocycloalkyl- C_1 - C_4 alkyl, cyano- C_1 - C_4 alkyl, C_1 - C_6 alkoxy- C_1 - C_4 alkyl, C_1 - C_6 alkylthio- C_1 - C_4 alkyl, C_1 - C_6 alkylsulfinyl- C_1 - C_4 alkyl, C_1 - C_6 alkylsulfonyl- C_1 - C_4 alkyl, hydroxy- C_1 - C_4 alkyl, C_1 - C_6 alkylcarbonyl- C_1 - C_4 alkyl, C_1 - C_6 alkoxycarbonyl, C_1 - C_6 alkoxy-carbonyl- C_1 - C_4 alkyl, C_1 - C_6 alkoxycarbonyl- C_1 - C_4 haloalkyl, C_1 - C_6 alkoxycarbonyl- C_1 - C_4 alkoxy, C_1 - C_6 alkylcarbonyloxy- C_1 - C_4 alkyl, C_1 - C_6 alkoxycarbonyloxy- C_1 - C_4 alkyl, C_1 - C_4 alkoxy- C_1 - C_2 alkoxy- C_1 - C_2 alkyl, C_1 - C_4 alkylaminocarbonyl, C_1 - C_6 alkylaminocarbonyl- C_1 - C_4 alkoxy, phenyl, phenoxy or by benzyloxy, wherein the phenyl ring of the last three definitions may

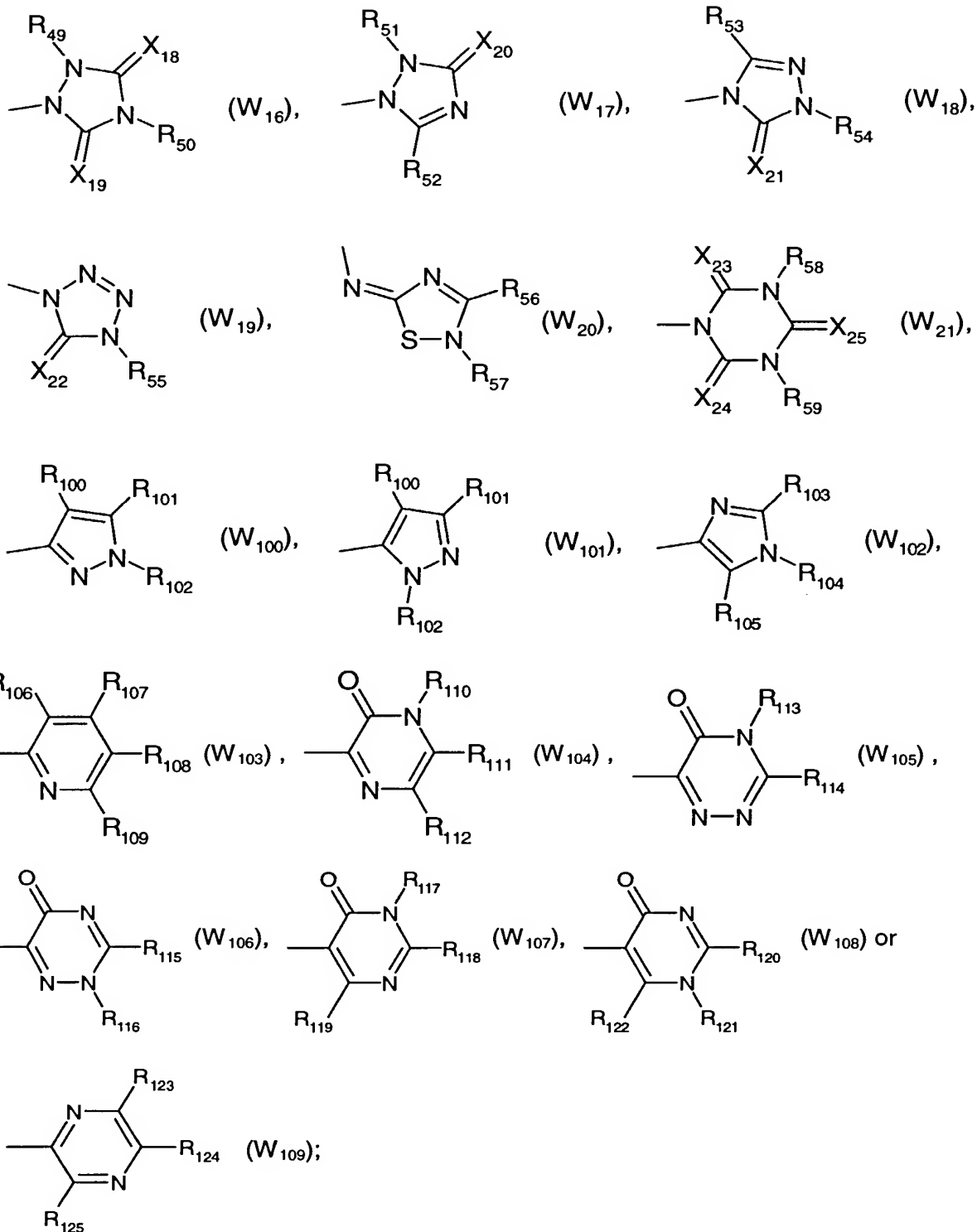
be substituted by halogen, methyl, trifluoromethyl, methylsulfonyl, methoxy, ethoxy or by cyano; or is phenyl-substituted C₂-C₄alkenyl or C₂-C₄alkynyl, wherein the phenyl group may be substituted by halogen, methyl, trifluoromethyl, methylthio, methylsulfinyl, methylsulfonyl, methoxy, ethoxy, cyano or by nitro;

R₃ is hydrogen, C₁-C₁₂alkyl, C₁-C₁₂haloalkyl, C₁-C₆alkoxycarbonyl, or phenyl which is unsubstituted or substituted by halogen, methyl, trifluoromethyl, methylthio, methylsulfinyl, methylsulfonyl, methoxy, ethoxy, cyano or by nitro;

R₄ is hydrogen or C₁-C₆alkyl;

W is a group





R₁₁ is hydrogen, C₁-C₃alkyl, halogen, C₁-C₃haloalkyl or cyano;

R₁₂ is C₁-C₃alkyl, C₁-C₃haloalkyl, C₁-C₃alkyl-S(O)_{n1}-, C₁-C₃haloalkyl-S(O)_{n1}- or cyano;

and

R₁₃ is hydrogen, C₁-C₃alkyl, C₁-C₃haloalkyl, allyl, propargyl or amino; or

R₁₂ and R₁₁ or R₁₂ and R₁₃ together form a C₃- or C₄-alkylene bridge which may be substituted by halogen, C₁-C₃haloalkyl or by cyano;

R₁₄ is hydrogen, C₁-C₃alkyl, halogen, C₁-C₃haloalkyl or cyano; and

R₁₅ is C₁-C₃alkyl, C₁-C₃haloalkyl, C₁-C₃alkyl-S(O)_{n2}-, C₁-C₃haloalkyl-S(O)_{n2}- or cyano; or

R₁₅ and R₁₄ together form a C₃- or C₄-alkylene bridge which may be substituted by halogen, C₁-C₃haloalkyl or by cyano;

R₁₆ is hydrogen, C₁-C₃alkyl, halogen, C₁-C₃haloalkyl, C₁-C₃alkoxy, C₁-C₃haloalkoxy, hydroxy, mercapto, C₁-C₃alkylthio, allylthio, propargylthio, C₁-C₃alkylsulfinyl, C₁-C₃alkylsulfonyl, amino, C₁-C₃alkylamino, di(C₁-C₃alkyl)amino, allylamino, propargylamino or cyano;

n₁ and n₂ are 0, 1 or 2;

R₁₇ is hydrogen, C₁-C₃alkyl, halogen or cyano; and

R₁₈ is C₁-C₃alkyl, halogen, C₁-C₃haloalkyl, C₁-C₃alkylthio, C₁-C₃alkylsulfinyl, C₁-C₃alkylsulfonyl or cyano; or

R₁₈ and R₁₇ together form a C₃- or C₄-alkylene or C₃- or C₄-alkenylene bridge, both of which may be substituted by halogen, C₁-C₃alkyl or by C₁-C₃haloalkyl;

R₁₉ is hydrogen, halogen, C₁-C₃alkyl, carboxyl, C₁-C₃alkoxycarbonyl or amino; or

R₁₉ and R₁₈ together form a C₃- or C₄-alkylene or C₃- or C₄-alkenylene bridge, both of which may be substituted by halogen, C₁-C₃alkyl or by C₁-C₃haloalkyl;

R₂₀ and R₂₁ are each independently of the other hydrogen or C₁-C₄alkyl; or

R₂₀ and R₂₁ together are a group $\begin{array}{c} \text{R}_{051} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{R}_{052} \end{array}$;

R₀₅₁ and R₀₅₂ are each independently of the other hydrogen or C₁-C₄alkyl; or

R₀₅₁ and R₀₅₂ together form a C₄- or C₅-alkylene bridge;

R₀₅₂ and R₂₂ together form a C₃alkylene bridge;

R₂₂ is hydrogen or C₁-C₃alkyl; or

R₂₂ and R₂₀ or R₂₂ and R₂₁ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by halogen, C₁-C₄alkyl, C₁-C₃haloalkyl, C₂-C₄alkenyl, C₁-C₃alkoxycarbonyl, C₁-C₃alkylcarbonyloxy, C₁-C₃alkylsulfonyloxy or by hydroxy;

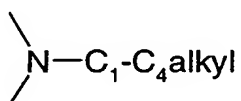
R₂₃ and R₂₄ are each independently of the other hydrogen, C₁-C₃alkyl, C₁-C₃haloalkyl or propargyl; or

R₂₃ and R₂₄ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by halogen, C₁-C₄alkyl, hydroxy, C₁-C₄alkoxy or by C₁-C₄alkoxy-C₁-C₄alkoxy;

R₂₅ is hydrogen, halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, C₁-C₄alkylthio, C₁-C₄haloalkylthio, C₁-C₄alkylsulfinyl, C₁-C₄haloalkylsulfinyl, C₁-C₄alkylsulfonyl, C₁-C₄haloalkylsulfonyl, hydroxy or cyano; and

R₂₆ is hydrogen, C₁-C₄alkyl or C₁-C₄haloalkyl; or

R₂₆ and R₂₅ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen,

sulfur, -S(O)-, -S(O)₂-,  or by -C(O)- and/or substituted by halogen, C₁-

C₄alkyl, C₁-C₃haloalkyl, C₂-C₄alkenyl, C₁-C₃alkoxycarbonyl, C₁-C₃alkylcarbonyloxy, C₁-C₃alkylsulfonyloxy or by hydroxy;

R₂₇ and R₂₈ are each independently of the other hydrogen or C₁-C₄alkyl; or

R₂₇ and R₂₈ together form a C₃-C₅alkylene bridge which may be substituted by halogen or by C₁-C₄alkyl and/or interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- or form a C₄alkenylene bridge which is unsubstituted or substituted by C₁-C₄alkyl;

R₂₉ and R₃₀ are each independently of the other hydrogen, C₁-C₄alkyl or C₁-C₄haloalkyl; or

R₂₉ and R₃₀ together form a C₃-C₅alkylene bridge which may be substituted by halogen or by C₁-C₄alkyl and/or interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)-;

R₃₁ is hydrogen, C₁-C₄alkyl or C₁-C₄haloalkyl; and

R₃₂ is hydrogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkylthio, C₁-C₄alkylsulfinyl, C₁-C₄alkylsulfonyl, cyano or nitro; or

R₃₁ and R₃₂ together form a C₃-C₅alkylene bridge which may be substituted by halogen or by C₁-C₄alkyl and/or interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- or form a C₄alkenylene bridge which is unsubstituted or substituted by C₁-C₄alkyl;

R₃₃ is hydrogen, C₁-C₃alkyl, halogen, C₁-C₃haloalkyl, hydroxy, C₁-C₃alkoxy, C₁-C₃haloalkoxy, mercapto, C₁-C₃alkylthio, C₁-C₃alkylsulfinyl, C₁-C₃alkylsulfonyl, amino, C₁-C₃alkylamino, C₁-C₃alkylcarbonylamino, C₁-C₃haloalkylcarbonylamino or cyano;

R₃₄ is C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄alkylthio;

R₃₆ is hydrogen, C₁-C₃alkyl, halogen, C₁-C₃haloalkyl or cyano; and

R₃₇ is C₁-C₃alkyl, C₁-C₃haloalkyl, C₁-C₃alkyl-S(O)_{n1}-, C₁-C₃haloalkyl-S(O)_{n1}- or cyano; or

R₃₇ and R₃₆ together form a C₃- or C₄-alkenylene bridge which may be substituted by halogen, C₁-C₃alkyl, C₁-C₃haloalkyl or by cyano;

R₃₈ is C₁-C₃alkyl; and

R₃₉ is hydrogen or C₁-C₃alkyl; or

R₃₉ and R₃₈ together form a C₂- or C₃-alkylene or C₂- or C₃-alkenylene bridge which is unsubstituted or substituted by C₁-C₄alkyl or form an -NH-CH₂-, -N=CH- or -N=N- bridge;

R₄₀ and R₄₁ are each independently of the other C₁-C₃alkyl or C₁-C₃haloalkyl; or

R₄₁ and R₄₀ together form a C₃-C₅alkylene bridge which is unsubstituted or substituted by halogen or by C₁-C₄alkyl;

R₄₂ is hydrogen, C₁-C₃alkyl, C₁-C₃haloalkyl, cyano or carboxyl;

R₄₃ is hydrogen, C₁-C₃alkyl, C₁-C₃haloalkyl, allyl or propargyl;

R₄₄ is hydrogen, C₁-C₃alkyl, halogen, C₁-C₃haloalkyl, hydroxy, mercapto, amino, C₁-C₃alkoxy, C₁-C₃alkylthio or di(C₁-C₄alkyl)amino;

R₄₅ is hydrogen, C₁-C₃alkyl, halogen or cyano;

R₄₆ is C₁-C₃alkyl, C₁-C₃haloalkyl or cyano;

R₄₇ is hydrogen, C₁-C₃alkyl or halogen;

R₄₈ is C₁-C₃alkyl or C₁-C₃haloalkyl;

R₄₉, R₅₀ and R₅₁ are each independently of the others hydrogen, C₁-C₄alkyl, propargyl or C₁-C₄haloalkyl;

R₅₂ is C₁-C₃alkyl, halogen, C₁-C₃haloalkyl, C₁-C₃alkoxy, C₁-C₃haloalkoxy, C₁-C₃alkylthio, C₁-C₃alkylsulfinyl, C₁-C₃alkylsulfonyl, amino or C₁-C₃alkylamino;

R₅₃ is C₁-C₃alkyl or C₁-C₃haloalkyl;

R₅₄ is C₁-C₃alkyl;

R₅₅ is hydrogen, C₁-C₃alkyl, propargyl or C₁-C₃haloalkyl;

R₅₆ is C₁-C₃alkyl, C₁-C₃haloalkyl, C₁-C₃alkylthio, C₁-C₃alkylsulfinyl or C₁-C₃alkylsulfonyl;
and

R₅₇ is C₁-C₃alkyl or C₁-C₃haloalkyl; or

R₅₇ and R₅₆ together form a C₂-C₄alkylene or C₂-C₄alkenylene bridge which both are unsubstituted or substituted by halogen or by C₁-C₄alkyl;

R₅₈ is hydrogen, C₁-C₃alkyl, C₁-C₃haloalkyl or amino;

R₅₉ is hydrogen, C₁-C₃alkyl or C₁-C₃haloalkyl;

R₁₀₀ is hydrogen, halogen, nitro, amino, cyano, C₁-C₃alkyl, C₂- or C₃-alkenyl or C₂- or C₃-alkynyl;

R₁₀₁ is hydrogen, halogen, nitro, amino, cyano, hydroxy, mercapto, C₁-C₃alkyl, C₁-C₃haloalkyl, C₂- or C₃-alkenyl, C₂- or C₃-alkynyl, C₁-C₃alkoxy, C₁-C₃haloalkoxy, C₁-C₃alkylthio, C₁-C₃alkylsulfinyl, C₁-C₃alkylsulfonyl, C₁-C₃haloalkylthio, C₁-C₃haloalkylsulfinyl, C₁-C₃haloalkylsulfonyl, FS(O)₂-, ClS(O)₂-, C₁-C₆alkylsulfonyloxy, C₁-C₆haloalkylsulfonyloxy, C₁-C₃alkylcarbonyl, HC(O)-, HOC(O)-, ClC(O)-, FC(O)-, C₁-C₃alkoxycarbonyl, H₂NC(O)- or H₂NC(S)-; and

R₁₀₂ is hydrogen, C₁-C₆alkyl, C₁-C₆alkyl substituted by cyano, HO-, HOC(O)-, C₁-C₃alkoxycarbonyl or by HC(O)-, or is C₃-C₆alkenyl, C₃-C₆alkynyl, C₃-C₆cycloalkyl, C₁-C₆haloalkyl or C₁-C₃alkylsulfonyl; or

when W is a group W₁₀₀,

R₁₀₂ and R₁₀₁ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen;

R₁₀₃ is hydrogen, halogen, nitro, amino, cyano, hydroxy, mercapto, C₁-C₃alkyl, C₁-C₃haloalkyl, C₂- or C₃-alkenyl, C₂- or C₃-alkynyl, C₁-C₃alkoxy, C₁-C₃haloalkoxy, C₁-C₃alkylthio, C₁-C₃alkylsulfinyl, C₁-C₃alkylsulfonyl, C₁-C₃haloalkylthio, C₁-C₃haloalkylsulfinyl, C₁-C₃haloalkylsulfonyl, FS(O)₂-, ClS(O)₂-, C₁-C₆alkylsulfonyloxy, C₁-C₆haloalkylsulfonyloxy, C₁-C₃alkylcarbonyl, HC(O)-, HOC(O)-, ClC(O)-, FC(O)-, C₁-C₃alkoxycarbonyl, H₂NC(O)- or H₂NC(S)-;

R₁₀₄ is hydrogen, C₁-C₆alkyl, C₁-C₆alkyl substituted by cyano, HO-, HOC(O)-, C₁-C₃alkoxy-carbonyl or by HC(O)-, or is C₃-C₆alkenyl, C₃-C₆alkynyl, C₃-C₆cycloalkyl, C₁-C₆haloalkyl or C₁-C₃alkylsulfonyl; and

R₁₀₅ is hydrogen, halogen, nitro, amino, cyano, C₁-C₃alkyl, C₂- or C₃-alkenyl or C₂- or C₃-alkynyl; or

R₁₀₄ and R₁₀₃ together form a C₃-C₅alkylene bridge or a C₄alkenylene bridge which both may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen;

R₁₀₆ is hydrogen, halogen, amino, nitro, hydroxy, C₁-C₃alkyl or C₁-C₃alkoxy;

R₁₀₇ is hydrogen, halogen, amino, hydroxy, C₁-C₃alkyl, C₁-C₃haloalkyl, HC(O)-, HOC(O)-, hydroxy-C₁-C₃alkyl, C₁-C₃alkoxy or C₁-C₃haloalkoxy; and

R₁₀₈ is hydrogen, halogen, nitro, amino, cyano, HC(O)-, HOC(O)-, H₂NC(O)-, H₂NC(S)-, hydroxy, mercapto, C₁-C₃alkyl, C₁-C₃haloalkyl, C₂- or C₃-alkenyl, C₁-C₃alkoxy, C₁-C₃haloalkoxy, C₁-C₃alkylcarbonyl, C₁-C₃alkoxycarbonyl, C₁-C₃alkylthio, C₁-C₃haloalkylthio, C₁-C₃alkylsulfinyl, C₁-C₃haloalkylsulfinyl, C₁-C₃alkylsulfonyl, C₁-C₃haloalkylsulfonyl, C₁-C₃alkylsulfonyloxy or C₁-C₃haloalkylsulfonyloxy; or

R₁₀₈ and R₁₀₇ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen;

R₁₀₉ is hydrogen, halogen, amino, hydroxy, C₁-C₃alkyl, C₁-C₃haloalkyl, HC(O)-, HOC(O)-, hydroxy-C₁-C₃alkyl, C₁-C₃alkoxy or C₁-C₃haloalkoxy; or

R₁₀₉ and R₁₀₈ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen;

R₁₁₀ is hydrogen, C₁-C₃alkyl, C₁-C₃haloalkyl, C₃-C₄alkenyl or C₃-C₄alkynyl;

R₁₁₁ is hydrogen, halogen, nitro, amino, cyano, HC(O)-, HOC(O)-, H₂NC(O)-, H₂NC(S)-, hydroxy, mercapto, C₁-C₃alkyl, C₁-C₃haloalkyl, C₂- or C₃-alkenyl, C₁-C₃alkoxy, C₁-C₃haloalkoxy, C₁-C₃alkylcarbonyl, C₁-C₃alkoxycarbonyl, C₁-C₃alkylthio, C₁-C₃haloalkylthio, C₁-C₃alkylsulfinyl, C₁-C₃haloalkylsulfinyl, C₁-C₃alkylsulfonyl, C₁-C₃haloalkylsulfonyl, C₁-C₃alkylsulfonyloxy or C₁-C₃haloalkylsulfonyloxy; and

R₁₁₂ is hydrogen, halogen, amino, hydroxy, C₁-C₃alkyl, C₁-C₃haloalkyl, HC(O)-, HOC(O)-, hydroxy-C₁-C₃alkyl, C₁-C₃alkoxy or C₁-C₃haloalkoxy; or

R₁₁₁ and R₁₁₀ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein the C₃-C₅alkylene bridge is bonded to the N atom of the pyrazinone *via* a CH₂ group; or

R₁₁₂ and R₁₁₁ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen;

R₁₁₃ is hydrogen, C₁-C₃alkyl, C₁-C₃haloalkyl, C₃-C₄alkenyl or C₃-C₄alkynyl; and

R₁₁₄ is hydrogen, halogen, nitro, amino, cyano, HC(O)-, HOC(O)-, H₂NC(O)-, H₂NC(S)-, hydroxy, mercapto, C₁-C₃alkyl, C₁-C₃haloalkyl, C₂- or C₃-alkenyl, C₁-C₃alkoxy, C₁-C₃haloalkoxy, C₁-C₃alkylcarbonyl, C₁-C₃alkoxycarbonyl, C₁-C₃alkylthio, C₁-C₃haloalkylthio, C₁-C₃alkylsulfinyl, C₁-C₃haloalkylsulfinyl, C₁-C₃alkylsulfonyl, C₁-C₃haloalkylsulfonyl, C₁-C₃alkylsulfonyloxy, C₁-C₃haloalkylsulfonyloxy, C₁-C₃alkylamino or di(C₁-C₃alkyl)amino; or

R₁₁₄ and R₁₁₃ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein the C₃-C₅alkylene bridge is bonded to the N atom of the triazinone *via* a CH₂ group;

R₁₁₅ is hydrogen, halogen, nitro, amino, cyano, HC(O)-, HOC(O)-, H₂NC(O)-, H₂NC(S)-, hydroxy, mercapto, C₁-C₃alkyl, C₁-C₃haloalkyl, C₂- or C₃-alkenyl, C₁-C₃alkoxy, C₁-C₃haloalkoxy, C₁-C₃alkylcarbonyl, C₁-C₃alkoxycarbonyl, C₁-C₃alkylthio, C₁-C₃haloalkylthio, C₁-C₃alkylsulfinyl, C₁-C₃haloalkylsulfinyl, C₁-C₃alkylsulfonyl, C₁-C₃haloalkylsulfonyl, C₁-C₃alkylsulfonyloxy or C₁-C₃haloalkylsulfonyloxy; and

R₁₁₆ is hydrogen, C₁-C₃alkyl, C₁-C₃haloalkyl, C₃-C₄alkenyl or C₃-C₄alkynyl; or

R₁₁₆ and R₁₁₅ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein the C₃-C₅alkylene bridge is bonded to the N atom of the triazinone *via* a CH₂ group;

R₁₁₇ is hydrogen, C₁-C₃alkyl, C₁-C₃haloalkyl, C₃-C₄alkenyl or C₃-C₄alkynyl;

R₁₁₈ is hydrogen, halogen, nitro, amino, cyano, HC(O)-, HOC(O)-, H₂NC(O)-, H₂NC(S)-, hydroxy, mercapto, C₁-C₃alkyl, C₁-C₃haloalkyl, C₂- or C₃-alkenyl, C₁-C₃alkoxy, C₁-C₃haloalkoxy, C₁-C₃alkylcarbonyl, C₁-C₃alkoxycarbonyl, C₁-C₃alkylthio, C₁-C₃haloalkylthio,

C₁-C₃alkylsulfinyl, C₁-C₃haloalkylsulfinyl, C₁-C₃alkylsulfonyl, C₁-C₃haloalkylsulfonyl, C₁-C₃alkylsulfonyloxy or C₁-C₃haloalkylsulfonyloxy; and

R₁₁₉ is hydrogen, halogen, amino, nitro, hydroxy, C₁-C₃alkyl or C₁-C₃alkoxy; or
R₁₁₈ and R₁₁₇ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein the C₃-C₅alkylene bridge is bonded to the N atom of the pyrimidinone *via* a CH₂ group;

R₁₂₀ is hydrogen, halogen, nitro, amino, cyano, HC(O)-, HOC(O)-, H₂NC(O)-, H₂NC(S)-, hydroxy, mercapto, C₁-C₃alkyl, C₁-C₃haloalkyl, C₂- or C₃-alkenyl, C₁-C₃alkoxy, C₁-C₃haloalkoxy, C₁-C₃alkylcarbonyl, C₁-C₃alkoxycarbonyl, C₁-C₃alkylthio, C₁-C₃haloalkylthio, C₁-C₃alkylsulfinyl, C₁-C₃haloalkylsulfinyl, C₁-C₃alkylsulfonyl, C₁-C₃haloalkylsulfonyl, C₁-C₃alkylsulfonyloxy or C₁-C₃haloalkylsulfonyloxy;

R₁₂₁ is hydrogen, C₁-C₃alkyl, C₁-C₃haloalkyl, C₃- or C₄-alkenyl or C₃- or C₄-alkynyl; and

R₁₂₂ is hydrogen, halogen, amino, nitro, hydroxy, C₁-C₃alkyl or C₁-C₃alkoxy; or
R₁₂₁ and R₁₂₀ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein the C₃-C₅alkylene bridge is bonded to the N atom of the pyrimidinone *via* a CH₂ group;

R₁₂₃ is hydrogen, C₁-C₃alkyl, halogen or C₁-C₃haloalkyl;

R₁₂₄ is hydrogen, halogen, nitro, amino, cyano, HC(O)-, HOC(O)-, H₂NC(O)-, H₂NC(S)-, hydroxy, mercapto, C₁-C₃alkyl, C₁-C₃haloalkyl, C₂- or C₃-alkenyl, C₁-C₃alkoxy, C₁-C₃haloalkoxy, C₁-C₃alkylcarbonyl, C₁-C₃alkoxycarbonyl, C₁-C₃alkylthio, C₁-C₃haloalkylthio, C₁-C₃alkylsulfinyl, C₁-C₃haloalkylsulfinyl, C₁-C₃alkylsulfonyl, C₁-C₃haloalkylsulfonyl, C₁-C₃alkylsulfonyloxy or C₁-C₃haloalkylsulfonyloxy; and

R₁₂₅ is hydrogen, C₁-C₃alkyl, halogen, hydroxy, C₁-C₃alkoxy, C₁-C₃haloalkoxy, C₁-C₃alkylthio, C₁-C₃alkylsulfinyl, C₁-C₃alkylsulfonyl, amino or cyano;

X₁, X₂, X₃, X₄, X₅, X₆, X₇, X₈, X₉, X₁₀, X₁₁, X₁₂, X₁₃, X₁₄, X₁₅, X₁₆, X₁₇, X₁₈, X₁₉, X₂₀, X₂₁, X₂₂, X₂₃, X₂₄ and X₂₅ are each independently of the others oxygen or sulfur; and

Y₁ and Y₂ are oxygen or sulfur,

or an agrochemically acceptable salt or tautomer, enantiomer or stereoisomer of such a compound of formula I.

2. A compound of formula I according to claim 1 wherein

R₁ is hydrogen, methyl or halogen;

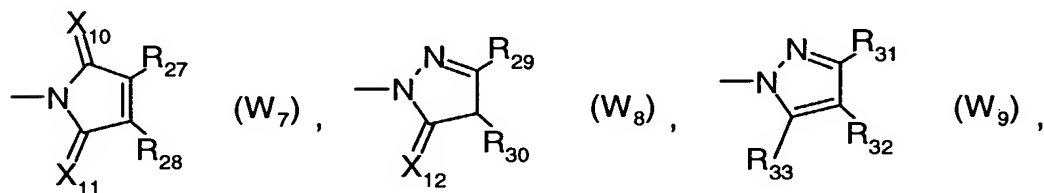
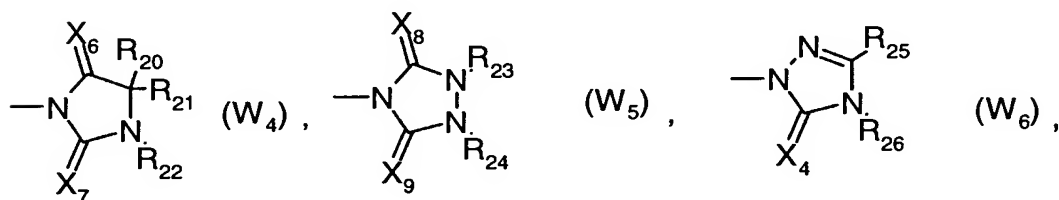
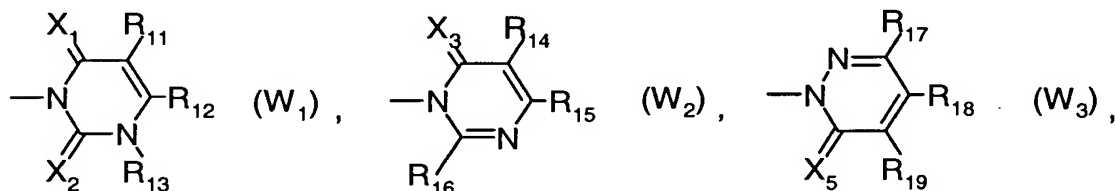
R₂ is hydrogen, C₁-C₁₂alkyl, C₁-C₁₂haloalkyl, C₁-C₁₂alkenyl, C₁-C₁₂alkynyl, C₁-C₁₂haloalkenyl, C₁-C₁₂haloalkynyl, C₁-C₆cycloalkyl-C₁-C₄alkyl, C₁-C₆halocycloalkyl-C₁-C₄alkyl, cyano-C₁-C₁₂alkyl, C₁-C₆alkoxy-C₁-C₄alkyl, C₁-C₄alkoxy-C₁-C₂alkoxy-C₁-C₂alkyl,

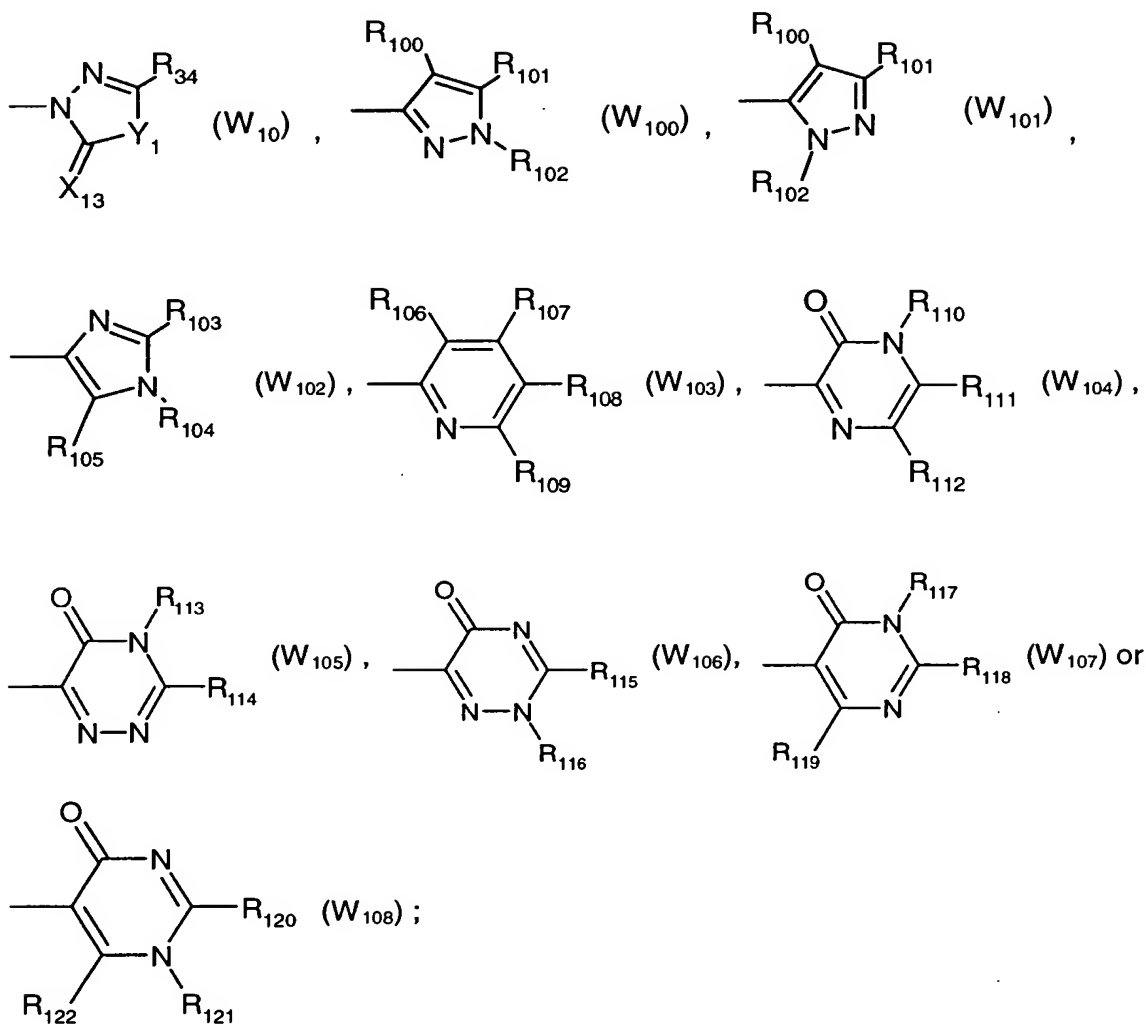
di(C₁-C₄alkoxy)C₁-C₂alkyl, C₁-C₆alkylthio-C₁-C₄alkyl, C₁-C₆alkylsulfinyl-C₁-C₄alkyl, C₁-C₆alkylsulfonyl-C₁-C₄alkyl, hydroxy-C₁-C₁₂alkyl, C₁-C₆alkylcarbonyl-C₁-C₄alkyl, C₁-C₆haloalkylcarbonyl-C₁-C₄alkyl, C₁-C₆alkoxycarbonyl-C₁-C₄alkyl, C₁-C₆alkoxycarbonyl-C₁-C₄haloalkyl, C₁-C₆alkoxycarbonyl-benzyl, C₁-C₆alkenyloxycarbonyl-C₁-C₄alkyl, C₁-C₆alkynyloxycarbonyl-C₁-C₄alkyl, C₁-C₆alkylcarbonyloxy-C₁-C₄alkyl, C₁-C₆alkenylcarbonyloxy-C₁-C₄alkyl, C₁-C₆cycloalkylcarbonyloxy-C₁-C₄alkyl, benzoyloxy-C₁-C₄alkyl, C₁-C₆alkoxycarbonyloxy-C₁-C₄alkyl, C₁-C₆alkylaminocarbonyl-C₁-C₄alkyl, C₁-C₆alkylaminocarbonyl-benzyl, or C₁-C₄alkyl substituted by phenyl or by heterocyclyl, wherein the phenyl and heterocyclyl group may be substituted one or more times by halogen, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkenyl, C₁-C₆alkynyl, C₁-C₆haloalkenyl, C₁-C₆haloalkynyl, C₁-C₆cycloalkyl-C₁-C₄alkyl, C₁-C₆halocycloalkyl-C₁-C₄alkyl, cyano-C₁-C₁₂alkyl, C₁-C₆alkoxy-C₁-C₄alkyl, C₁-C₆alkylthio-C₁-C₄alkyl, C₁-C₆alkylsulfinyl-C₁-C₄alkyl, C₁-C₆alkylsulfonyl-C₁-C₄alkyl, hydroxy-C₁-C₁₂alkyl, C₁-C₆alkylcarbonyl-C₁-C₄alkyl, C₁-C₆alkoxycarbonyl-C₁-C₄alkyl, C₁-C₆alkoxycarbonyl-C₁-C₄haloalkyl, C₁-C₆alkylcarbonyloxy-C₁-C₄alkyl, C₁-C₆alkoxycarbonyloxy-C₁-C₄alkyl, C₁-C₄alkoxy-C₁-C₂alkoxy-C₁-C₂alkyl or by phenyl;

R₃ is hydrogen, C₁-C₁₂alkyl, C₁-C₁₂haloalkyl or unsubstituted or substituted phenyl;

R₄ is hydrogen or C₁-C₆alkyl;

W is a group





R₁₁ is hydrogen, C₁-C₃alkyl, halogen, C₁-C₃haloalkyl or cyano;

R₁₂ is C₁-C₃alkyl, C₁-C₃haloalkyl, C₁-C₃alkyl-S(O)_{n1}-, C₁-C₃haloalkyl-S(O)_{n1}- or cyano;
and

R₁₃ is C₁-C₃alkyl, C₁-C₃haloalkyl or amino; or

R₁₂ and R₁₁ or R₁₂ and R₁₃ together form a C₃- or C₄-alkylene bridge which may be substituted by halogen, C₁-C₃haloalkyl or by cyano;

R₁₄ is hydrogen, C₁-C₃alkyl, halogen, C₁-C₃haloalkyl or cyano; and

R₁₅ is C₁-C₃alkyl, C₁-C₃haloalkyl, C₁-C₃alkyl-S(O)_{n2}-, C₁-C₃haloalkyl-S(O)_{n2}- or cyano; or
R₁₅ and R₁₄ together form a C₃- or C₄-alkylene bridge which may be substituted by halogen, C₁-C₃haloalkyl or by cyano;

R₁₆ is hydrogen, C₁-C₃alkyl, halogen, C₁-C₃haloalkyl, C₁-C₃alkoxy, C₁-C₃haloalkoxy, C₁-C₃alkylthio, C₁-C₃alkylsulfinyl, C₁-C₃alkylsulfonyl or cyano;

n₁ and n₂ are 0, 1 or 2;

R₁₇ is hydrogen, C₁-C₃alkyl, halogen or cyano; and

R₁₈ is C₁-C₃alkyl, halogen, C₁-C₃haloalkyl, C₁-C₃alkylthio, C₁-C₃alkylsulfinyl, C₁-C₃alkylsulfonyl or cyano; or

R₁₈ and R₁₇ together form a C₃- or C₄-alkylene or C₃- or C₄-alkenylene bridge, both of which may be substituted by halogen, C₁-C₃alkyl or by C₁-C₃haloalkyl;

R₁₉ is hydrogen, halogen, C₁-C₃alkyl or amino; or

R₁₉ and R₁₈ together form a C₃- or C₄alkylene or C₃- or C₄-alkenylene bridge, both of which may be substituted by halogen, C₁-C₃alkyl or C₁-C₃haloalkyl;

R₂₀ and R₂₁ are each independently of the other hydrogen or C₁-C₄alkyl; or

R₂₀ and R₂₁ together are a group $\begin{array}{c} \text{R}_{051} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{R}_{052} \end{array}$;

R₀₅₁ and R₀₅₂ are each independently of the other C₁-C₄alkyl; or

R₀₅₁ and R₀₅₂ together form a C₄- or C₅-alkylene bridge;

R₀₅₁ and R₂₂ together form a C₃alkylene bridge;

R₂₂ is hydrogen or C₁-C₃alkyl; or

R₂₂ and R₂₀ or R₂₂ and R₂₁ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen or by -C(O)- and/or substituted by halogen, C₁-C₄alkyl, C₁-C₃haloalkyl, C₂-C₄alkenyl, C₁-C₃alkoxycarbonyl, C₁-C₃alkylcarbonyloxy, C₁-C₃alkylsulfonyloxy or by hydroxy;

R₂₃ is hydrogen, C₁-C₃alkyl or C₁-C₃haloalkyl; or

R₂₃ and R₂₄ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)-;

R₂₅ is hydrogen, halogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy, C₁-C₄haloalkoxy, C₁-C₄alkylthio, C₁-C₄haloalkylthio, C₁-C₄alkylsulfinyl, C₁-C₄haloalkylsulfinyl, C₁-C₄alkylsulfonyl, C₁-C₄haloalkylsulfonyl or cyano; and

R₂₆ is hydrogen, C₁-C₄alkyl or C₁-C₄haloalkyl; or

R₂₆ and R₂₅ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen or by -C(O)- and/or substituted by halogen, C₁-C₄alkyl, C₁-C₃haloalkyl, C₂-C₄alkenyl, C₁-C₃alkoxycarbonyl, C₁-C₃alkylcarbonyloxy, C₁-C₃alkylsulfonyloxy or by hydroxy;

R₂₇ and R₂₈ are each independently of the other hydrogen or C₁-C₄alkyl; or

R₂₇ and R₂₈ together form a C₃-C₅alkylene bridge or a C₄alkenylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)-;

R₂₉ and R₃₀ are each independently of the other hydrogen or C₁-C₄alkyl; or

R₂₉ and R₃₀ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)-;

R₃₁ is hydrogen, C₁-C₄alkyl or C₁-C₄haloalkyl; and

R₃₂ is hydrogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkylthio, C₁-C₄alkylsulfinyl, C₁-C₄alkylsulfonyl, cyano or nitro; or

R₃₁ and R₃₂ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)-;

R₃₃ is hydrogen, C₁-C₃alkyl, halogen, C₁-C₃haloalkyl, C₁-C₃alkoxy, C₁-C₃haloalkoxy, C₁-C₃alkylthio, C₁-C₃alkylsulfinyl, C₁-C₃alkylsulfonyl, amino, C₁-C₃alkylamino, C₁-C₃alkylcarbonylamino, C₁-C₃haloalkylcarbonylamino or cyano;

R₃₄ is C₁-C₄alkyl, C₁-C₄haloalkyl, C₁-C₄alkoxy or C₁-C₄alkylthio;

R₁₀₀ is hydrogen, halogen, nitro, amino, cyano, C₁-C₃alkyl, C₂- or C₃-alkenyl or C₂- or C₃-alkynyl;

R₁₀₁ is hydrogen, halogen, nitro, amino, cyano, hydroxy, mercapto, C₁-C₃alkyl, C₁-C₃haloalkyl, C₂- or C₃-alkenyl, C₂- or C₃-alkynyl, C₁-C₃alkoxy, C₁-C₃haloalkoxy, C₁-C₃alkylthio, C₁-C₃alkylsulfinyl, C₁-C₃alkylsulfonyl, C₁-C₃haloalkylthio, C₁-C₃haloalkylsulfinyl, C₁-C₃haloalkylsulfonyl, FS(O)₂-, ClS(O)₂-, C₁-C₆alkylsulfonyloxy, C₁-C₆haloalkylsulfonyloxy, C₁-C₃alkylcarbonyl, HC(O)-, HOC(O)-, ClC(O)-, FC(O)-, C₁-C₃alkoxycarbonyl, H₂NC(O)- or H₂NC(S)-;

R₁₀₂ is hydrogen, C₁-C₆alkyl, C₃-C₆alkenyl, C₃-C₆alkynyl, C₃-C₆cycloalkyl, C₁-C₆haloalkyl, C₁-C₃alkylsulfonyl, or C₁-C₆alkyl which may be substituted by cyano, HO-, HOC(O)-, C₁-C₃-alkoxycarbonyl or by HC(O)-; or,

when W is a group W₁₀₀,

R₁₀₂ and R₁₀₁ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen;

R₁₀₃ is as defined for R₁₀₁;

R₁₀₄ is as defined for R₁₀₂;

R₁₀₅ is as defined for R₁₀₀;

R₁₀₆ is hydrogen, halogen, amino, nitro, hydroxy, C₁-C₃alkyl or C₁-C₃alkoxy;

R₁₀₇ is hydrogen, halogen, amino, hydroxy, C₁-C₃alkyl, C₁-C₃haloalkyl, HC(O)-, HOC(O)-, hydroxy-C₁-C₃alkyl, C₁-C₃alkoxy or C₁-C₃haloalkoxy; and

R₁₀₈ is hydrogen, halogen, nitro, amino, cyano, HC(O)-, HOC(O)-, H₂NC(O)-, H₂NC(S)-, hydroxy, HS-, C₁-C₃alkyl, C₁-C₃haloalkyl, C₂- or C₃-alkenyl, C₁-C₃alkoxy, C₁-C₃haloalkoxy, C₁-C₃alkylcarbonyl, C₁-C₃alkoxycarbonyl, C₁-C₃alkylthio, C₁-C₃haloalkylthio, C₁-C₃alkylsulfinyl, C₁-C₃haloalkylsulfinyl, C₁-C₃alkylsulfonyl, C₁-C₃haloalkylsulfonyl, C₁-C₃alkylsulfonyloxy or C₁-C₃haloalkylsulfonyloxy;

R₁₀₉ is as defined for R₁₀₇;

R₁₀₇ and R₁₀₈ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen;

R₁₀₈ and R₁₀₉ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen;

R₁₁₀ is hydrogen, C₁-C₃alkyl, C₁-C₃haloalkyl, C₃-C₄alkenyl or C₃-C₄alkynyl;

R₁₁₁ is as defined for R₁₀₈;

R₁₁₂ is as defined for R₁₀₉;

R₁₁₁ and R₁₁₂ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen;

R₁₁₀ and R₁₁₁ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein a CH₂ group is bonded to the N atom of the pyrazinone;

R₁₁₃ is as defined for R₁₁₀;

R₁₁₄ is as defined for R₁₀₈;

R₁₁₃ and R₁₁₄ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein a CH₂ group is bonded to the N atom of the triazinone;

R₁₁₅ is as defined for R₁₀₈;

R₁₁₆ is as defined for R₁₁₀;

R₁₁₅ and R₁₁₆ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein a CH₂ group is bonded to the N atom of the triazinone;

R₁₁₇ is as defined for R₁₁₀;

R₁₁₈ is as defined for R₁₀₈;

R₁₁₉ is as defined for R₁₀₆;

R₁₁₇ and R₁₁₈ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein a CH₂ group is bonded to the N atom of the pyrimidinone;

R₁₂₀ is as defined for R₁₀₈;

R₁₂₁ is as defined for R₁₁₀;

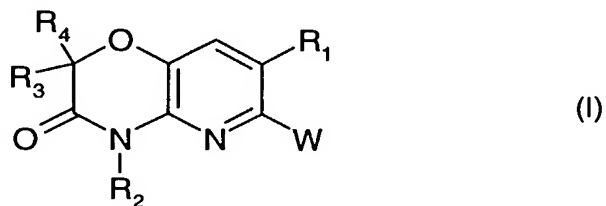
R₁₂₂ is as defined for R₁₀₆;

R₁₂₁ and R₁₂₀ together form a C₃-C₅alkylene bridge which may be interrupted by oxygen, sulfur, -S(O)-, -S(O)₂- or by -C(O)- and/or substituted by hydroxy or by halogen, wherein a CH₂ group is bonded to the N atom of the pyrimidinone;

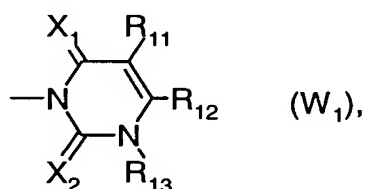
X₁, X₂, X₃, X₄, X₅, X₆, X₇, X₈, X₉, X₁₀, X₁₁, X₁₂ and X₁₃ are each independently of the others oxygen or sulfur; and

Y₁ is oxygen or sulfur.

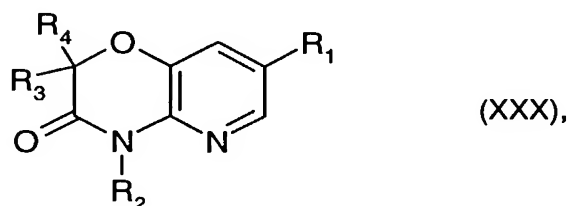
3. A process for the preparation of compounds of formula I according to claim 1, which process comprises, for the preparation of compounds of formula I



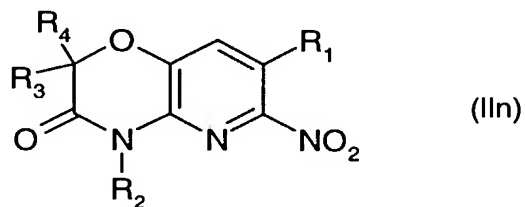
wherein R_1 , R_2 , R_3 and R_4 are as defined in claim 1 and W is a group W_1



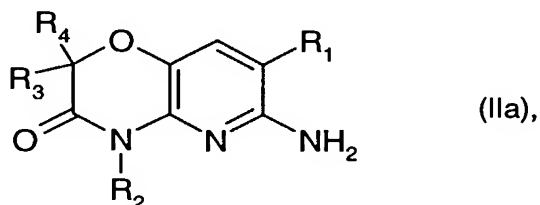
wherein R_{11} , R_{12} , R_{13} , X_1 and X_2 are as defined in claim 1, converting a compound of formula XXX



wherein R_1 , R_2 , R_3 and R_4 are as defined, by means of aromatic nitration, into the compound of formula IIa

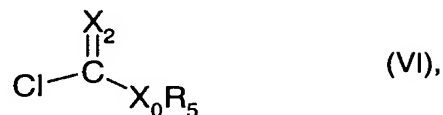


and subjecting that compound to reduction to yield the compound of formula IIa

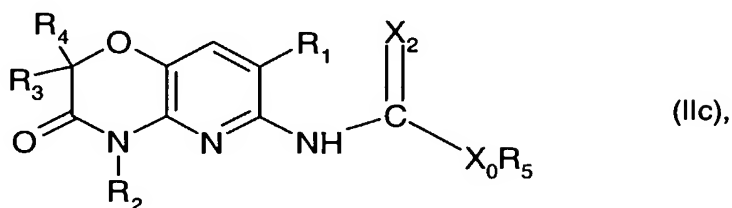


which is either

a) reacted with a compound of formula VI

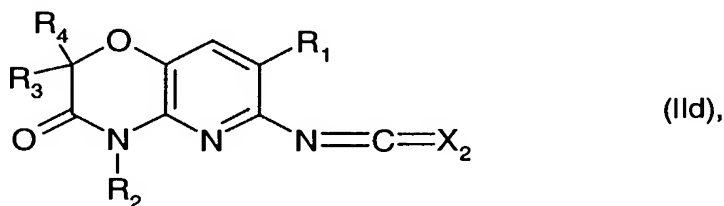


wherein X_2 is as defined in claim 1, X_0 is oxygen, sulfur or amino and R_5 is C_1 -Calkyl, to form the compound of formula IIc

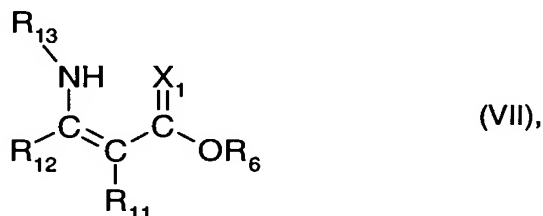


wherein R_1 , R_2 , R_3 , R_4 , R_5 , X_0 and X_2 are as defined, or

b) treated with phosgene ($\text{X}_2=\text{O}$) or thiophosgene ($\text{X}_2=\text{S}$) of formula $\text{C}(\text{X}_2)\text{Cl}_2$ or oxalyl chloride, to obtain the compound of formula IIId

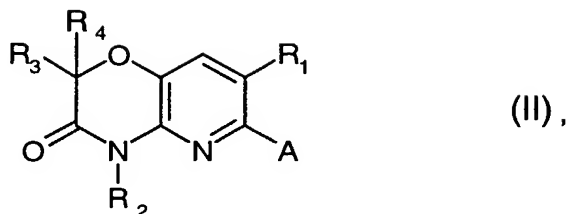


wherein R_1 , R_2 , R_3 , R_4 and X_2 are as defined, and condensing and cyclising the compounds of formulae IIc and IIId thereby obtained with an enamine of formula VII

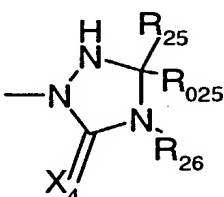


wherein R_{11} , R_{12} , R_{13} and X_1 are as defined and R_6 is C_1 - C_4 alkyl, in an inert solvent in the presence of from 0.01 to 1.5 equivalents of a suitable base, and then, optionally, further functionalising the substituents X_1 , X_2 , R_1 , R_2 , R_{11} and R_{13} according to their definitions.

4. A compound of formula II



wherein R_1 to R_4 are as defined for formula I and A is fluorine, C_1 - C_4 alkylthio, C_1 - C_4 alkylsulfonyl, phenylthio, phenylsulfonyl, C_1 - C_4 alkylsulfonyloxy, trifluoromethylsulfonyloxy, hydroxy, nitro, amino, isocyanato, isothiocyanato, hydrazino, a group $NHC(X_2)X_0R_5$, $NHC(X_7)X_0R_5$, $NHC(X_8)X_0R_5$, $NHC(X_9)X_0R_5$, $NHC(X_3)R_{16}$, $NHN=C(R_{17})C(O)R_{18}$, $NHC(X_7)N(R_{22})C(R_{20})R_{21}C(X_6)OR_9$, $NHC(X_9)NR_{24}NR_{23}C(X_8)OR_{10}$, $NHC(X_8)NR_{23}NHR_{24}$, $NHN=C(R_{25})COOH$, $NHN=C(R_{25})R_{025}$, $N(C(X_4)-NHR_{26})N=CR_{25}R_{025}$, $N(C(X_4)NHR_{26})NH_2$, $NHN=C(R_{25})N(R_{26})C(X_4)OR_{84}$, $N(C(X_4)NHR_{26})NHC(O)OR_{84}$, $N(C(X_{19})NHR_{50})NHC(O)OR_{84}$, $NHC(X_{12})NHR_{26}$, $NHC(O)C(R_{28})=C(R_{27})C(O)OR_{85}$, $NHC(=NR_{39})NHR_{38}$, $NHC(Y_2)NR_{40}NHR_{41}$, $NHC(Y_2)NR_{40}NR_{41}C(O)OR_9$, $NHN=C(R_{42})C(O)NHR_{43}$, $NHN=C(R_{42})C(O)N(R_{43})C(O)OR_{85}$, $N(R_{43})COOR_{85}$, $NHC(R_{53})=NNHC(X_{21})OR_{86}$, $NHC(S)NHC(=NR_{57})R_{56}$, $NHC(X_{23})NHR_{58}C(X_{25})NHR_{59}$, $N(C(X_{24})NHR_{59})C(X_{23})X_0R_5$, ethyl, vinyl, ethynyl, $C\equiv CC(O)OR_{86}$, $C\equiv CC(O)R_{87}$, acyl, formyl, cyano, carboxy, $C(O)OR_{89}$, $C(O)C(O)OR_{90}$,

$C(O)CH_2COOR_{91}$, $C(O)CH_2C(O)R_{88}$, cyanomethyl, $B(OH)_2$ or , wherein

R_{16} , R_{17} , R_{18} , R_{20} , R_{21} , R_{22} , R_{23} , R_{24} , R_{25} , R_{26} , R_{27} , R_{28} , R_{38} , R_{39} , R_{40} , R_{41} , R_{42} , R_{43} , R_{50} , R_{53} , R_{56} and R_{57} are as defined in claim 1; R_5 , R_9 , R_{025} , R_{84} , R_{86} , R_{89} , R_{90} and R_{91} are each independently of the others C_1 - C_4 alkyl or phenyl; R_{10} and R_{85} are hydrogen or C_1 - C_4 alkyl; R_{87} and R_{88} are C_1 - C_4 alkyl, formyl, $CH(C_1$ - C_4 alkoxy) or C_1 - C_4 haloalkyl; X_1 , X_2 , X_3 , X_4 , X_6 , X_7 , X_8 , X_9 , X_{12} , X_{19} , X_{21} and Y_2 are oxygen or sulfur; and X_0 is oxygen, sulfur or amino.

5. A herbicidal and plant-growth-inhibiting composition, comprising a herbicidally effective amount of a compound of formula I on an inert carrier.

6. A herbicidal and plant-growth-inhibiting composition according to claim 5, comprising at least one further co-herbicide as additional component.

7. A method of controlling undesired plant growth, which method comprises applying a compound of formula I, or a composition comprising such a compound, in a herbicidally effective amount to plants or to the locus thereof.

8. Use of a composition according to claim 5 in the control of undesired plant growth.